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PROBABILITY AND CRITICAL POTENTIALS FOR THE FORMATION OF MULTIPLY CHARGED IONS IN HG VAPOR BY ELECTRON IMPACT

By Walker Bleakney
Physical Laboratory, University of Minnesota

(Received December 15, 1929).

Abstract

With a type of apparatus previously reported the procedure is described for measuring the probability of the formation of multiply charged ions in mercury vapor as a function of the velocity of the incident electron.

Critical potentials for the formation of multiply charged ions. New results together with those of an earlier paper place the minimum or ionizing potentials for the formation of Hg^+, Hg^{2+}, Hg^{3+}, H^{4+}, and Hg^{5+} by a single impact at 10.4, 30, 71, 143, and 225 volts respectively. A brief correlation of these results with those of other observers is given.

Relative numbers of multiply charged ions. A set of curves is given showing the fraction of the total positive ion current carried by each type of ion as a function of the electron velocity. Another set of curves shows the fraction of the total number of ions carrying one, two, three, four, and five charges. The fraction for Hg^+ drops to a nearly constant value of 78 percent while the value for Hg^{2+} approaches 16 percent of the total number beyond 150 volts. At 400 volts the values for the five ions in order are 77, 16.5, 4.4, 1.3 and 0.8 percent respectively.

Quantitative measure of the number of ions produced and effective cross-sectional area of the Hg atom. Curves are given representing the number, N, of each type of ion, per electron, per cm path, per mm pressure at 0°C as a function of the electron velocity. The values of N for Hg^+, Hg^{2+}, Hg^{3+}, and Hg^{4+} have maxima of 20.8, 3.2, 0.72, 0.15 at 50, 115, 210, and 400 volts respectively. The effective cross-sectional area of the Hg atom toward an ionizing collision of a given type is obtained by dividing the appropriate value of N by the number of molecules per cc. The maximum value of this area for Hg^+ is about 60 percent of the kinetic theory value.

A discussion is given of the meaning of the area under the peaks in the e/m analysis curves and its effect on the accuracy of the interpretation of the data.

I. Introduction

BEFORE our knowledge of the probability of ionization in gases by electron impact can be complete it is necessary to investigate the critical potentials for the formation of multiply charged ions, and the effective cross-sectional area of the molecule or atom toward an ionizing collision as a function of the energy of the incident electron. Heretofore the types of apparatus used by investigators in this field have been such that the total number of unit positive charges was observed and not the actual number of ions formed since

an ion may carry several positive charages. It is important, therefore, to study separately the probability of the formation of ions having one, two, three, or more charges. Until recently no direct experimental method had been devised capable of such an investigation. The success of any method requires that only the primary products be examined, that is, the pressure of the gas must be such that there is little chance of an electron colliding twice and the current density of electrons must be so low that there is also little chance of an ion being struck a second time. The scheme proposed in a recent paper[1] lends itself very well to work of this kind. As yet a study has been made of mercury vapor only. A preliminary report[2] of some of the results has already been made.

II. Apparatus and Procedure

The apparatus used in the present experiment has already been described[1] in considerable detail and the reader is referred to this paper for the principles and details of the design. A plan view is shown in Figs. 1 and 2 for convenience in the discussions which follow.

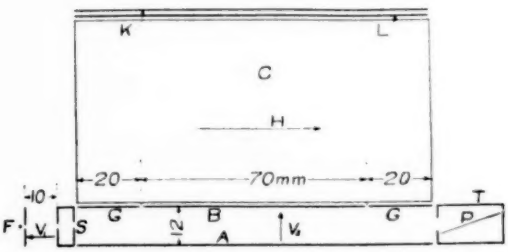

Fig. 1. Side view of apparatus.

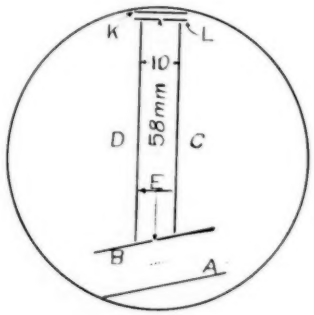

Fig. 2. End view.

The pressure of the mercury vapor was controlled by regulating the temperature of a trap in the exhaust line containing liquid mercury. The data for the pressure of the vapor corresponding to the temperatures used were taken from the International Critical Tables. The best temperature at which to work was found to be in the neighborhood of -20°C or a pressure of 1.81×10^{-5} mm Hg. Temperatures in this region were maintained either by a mixture of NaCl and ice or by solid CCl_4. The latter melts at -24°C. The temperature of the ionization chamber was measured by means of a thermocouple and was always found to be about 45°C. Since the mean free path of the atoms was much greater than the diameter of the connecting tube a pressure correction for diffusion was made to get the true pressure in the tube.

The electron current required in most cases was about 3×10^{-7} amperes. It was measured by means of a galvanometer of 4,000 megohms sensitivity. A potential (usually about 90 volts) was applied to the plate P positive with respect to the surrounding box of a magnitude sufficient to give a saturation current. The galvanometer measured the current to the box and plate com-

[1] W. Bleakney, Phys. Rev. **34**, 157 (1929).
[2] W. Bleakney, Phys. Rev. **35**, 123 (1930).

bined, thus obviating any correction due to ions being formed inside the box. It is believed that secondary electrons escaping from this arrangement were quite negligible. The positive ion current arriving at the plate B was measured with a Leeds and Northrup galvanometer of 110,000 megohms sensitivity. Saturation current to this plate was observed with a field V_2 as low as 0.3 volts per cm. The field strength used for the final runs was 3.3 volts per cm. The current to the plate K was measured with a Compton electrometer at a sensitivity of 2000 mm per volt. For the larger currents a direct deflection was observed by shunting the instrument with India ink resistances. For very small currents the time required to deflect through a given distance on the scale was measured.

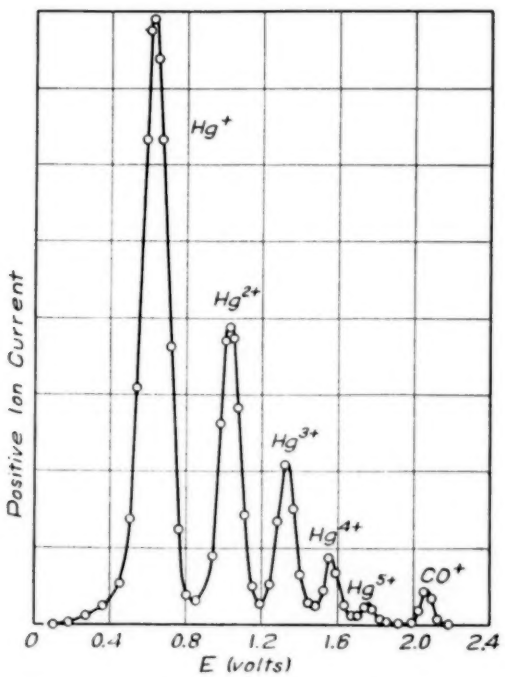

Fig. 3. A typical e/m analysis curve. $V_1 = 350$ volts. $p = 1.8 \times 10^{-5}$ mm Hg.

A set of preliminary runs was taken at various values of the field V_2. It was found that the relative sizes of the peaks remained unchanged between 1.2 and 3.5 volts per cm. A second set of preliminary runs was taken at various pressures, the results showing that the effects of scattering and neutralization were negligible at the pressures finally used. The final set of runs was then taken at electron velocities ranging from 20 to 500 volts.

III. Results

In Fig. 3 is shown a curve typical of a large number obtained with the apparatus. The electrometer current is plotted as a function of the crossed field E. In this instance the accelerating potential for the electrons V_1 was set at 350 volts, the drawing out field V_2 at 3.3 volts per cm, and the pressure was that corresponding to saturated mercury vapor at $-20°$C or 1.8×10^{-5} mm

Hg. The magnetic field furnished by the solenoid amounted to 400 gauss. The curve distinctly reveals the five mercury ions Hg^+, Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+}. Only one impurity shows up to any extent and its ionization potential was found to be 14.5 volts. It seems certain then that it is a singly charged ion and its position indicates a molecular weight of 28. These two facts are strong evidence for its being a CO^+ ion.

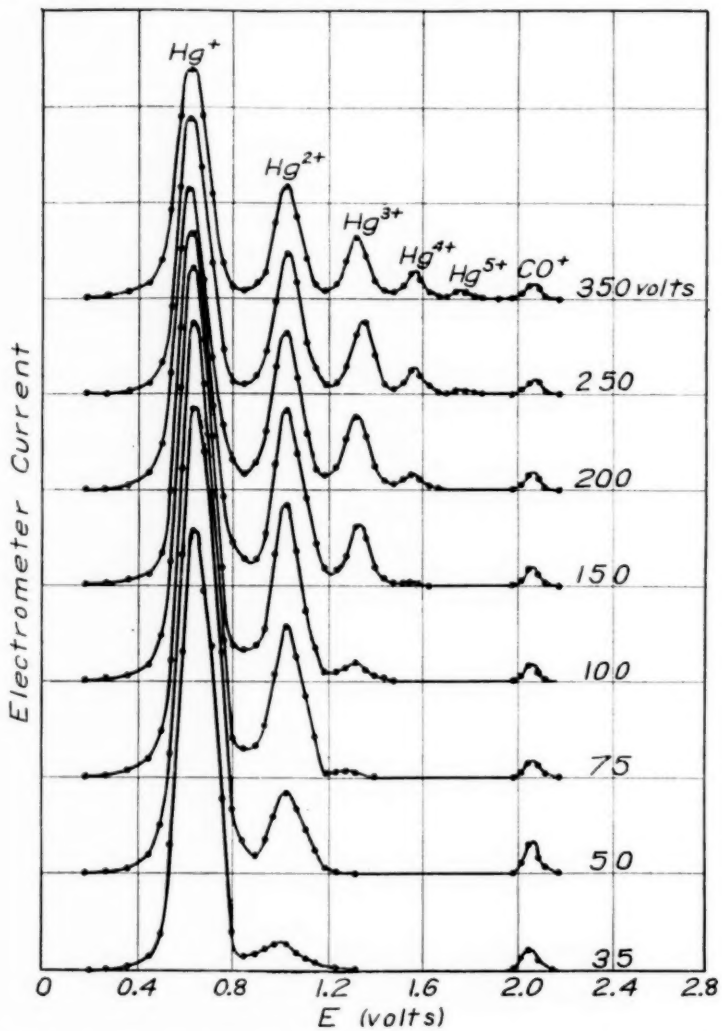

Fig. 4. A series of e/m analysis curves taken at various electron velocities.

Figure 4 illustrates a series of curves taken at electron velocities ranging from 35 to 350 volts. The ordinates of the different curves have been reduced to correspond to the same pressure and the same electron current throughout.

Critical potentials for the formation of multiply charged ions at single impact. If the areas under the peaks are plotted as a function of the electron velocity and the curves extrapolated to zero area the minimum or critical potentials for the formation of the different ions at a single collision are obtained. These

values may be called the ionization potentials for single impact. To the four values reported in the first paper[1] there is now added a fifth. The curves are shown in Fig. 5. The ionization potential for Hg^{5+} was difficult to determine with any accuracy because of the proximity of the Hg^{4+} peak and a very

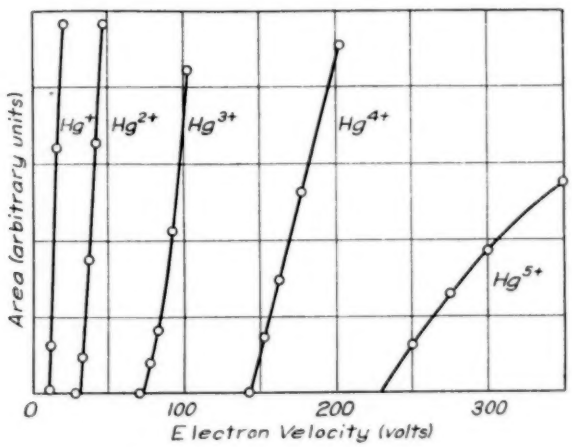

Fig. 5. Curves showing the ionization potentials at single impact.

slight impurity which coincided with the Hg^{5+} peak. Assuming the value of Hg^{+} to be 10.4 volts the values, with the estimated probable errors, of Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+} are placed at 30 ± 1, 71 ± 2, 143 ± 3, and 225 ± 5 volts respectively. There has been observed only slight evidence for the Hg^{6+} ion while Hg^{7+} and Hg^{8+}, if any are formed, are completely masked by the CO^{+} impurity.

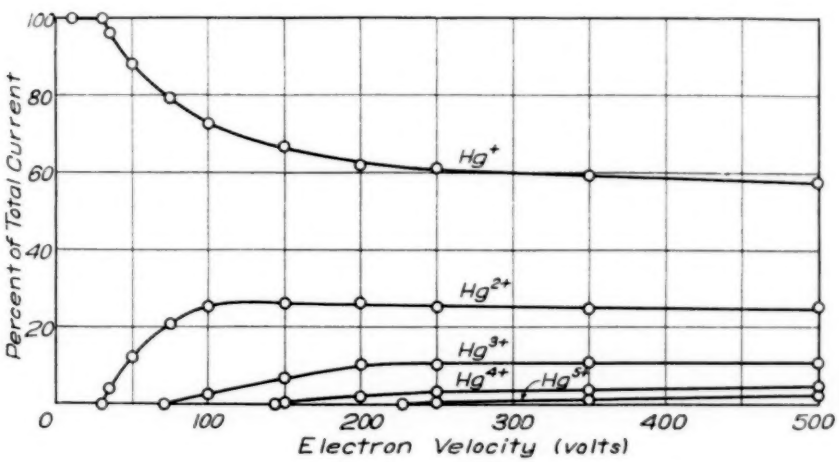

Fig. 6. Percent of total current carried by each type of ion.

Relative numbers of multiply charged ions. It will be assumed that the area under each peak of the e/m analysis curves is proportional to the current due to that particular type of ion and the validity of this assumption will be examined later. The curves of Fig. 6 representing the fractions of the total

current due to the different ions are obtained by plotting the area under each peak divided by the total area as a function of the electron velocity. Between 10.4 and 30 volts the positive ion current is 100 percent singly charged, and the effect of the appearance of the other ions is to lower this value to a nearly

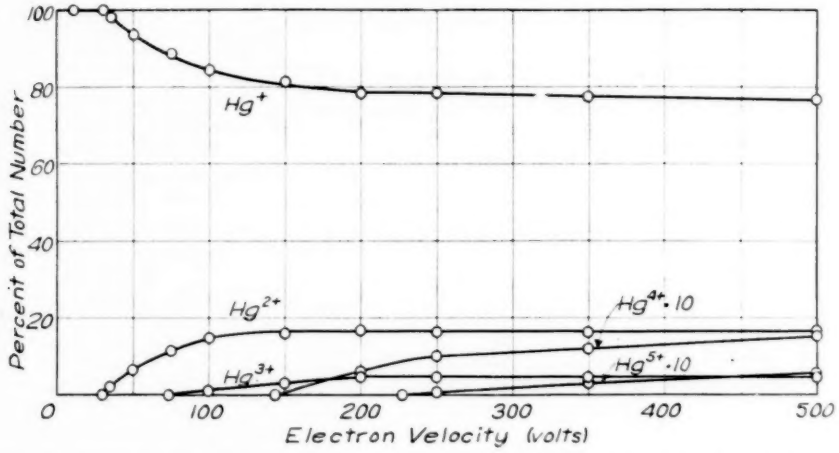

Fig. 7. Percent of total number of ions having one, two, three, four and five charges.

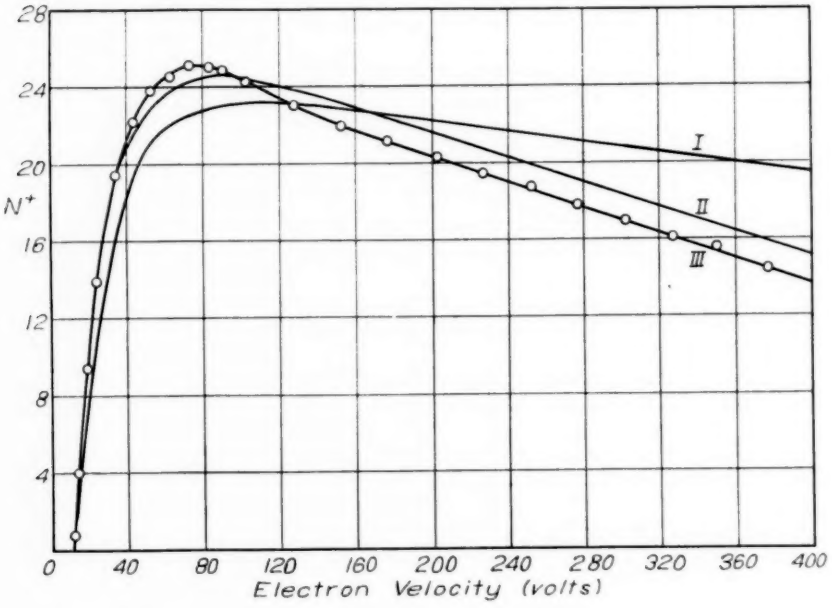

Fig. 8. Total number of positive charges, N^+, per electron per cm path per mm pressure at 0°C.

constant one of 59 percent at the higher velocities. The fractions of the total current due to Hg^{2+} and Hg^{3+} reach maximum values of 27 and 11 percent respectively.

To find the relative abundance of the different ions in *number* it is necessary to consider the total area under the first peak, one half the area under the

second, one third the area under the third, and so forth, as fractions of the sum. The curves of Fig. 7 show the results of this calculation. The ordinates for the fourth and fifth ions are here multiplied by 10. It will be noticed, for instance, that while at 300 volts the current due to Hg^+ is only 60 percent of the total yet 78 percent of the ions actually formed are singly charged.

Quantitative measure of the number of ions and the effective cross-sectional area of the Hg atom. As has been stated before the total number of positive charges arriving at the plate B was measured. Let the number of positive charges formed per electron per cm path per mm pressure at 0°C be denoted by N^+.

The values of N^+ are indicated in Fig. 8 as a function of the electron velocity. The curves of two other observers are shown for comparison. Curve I,

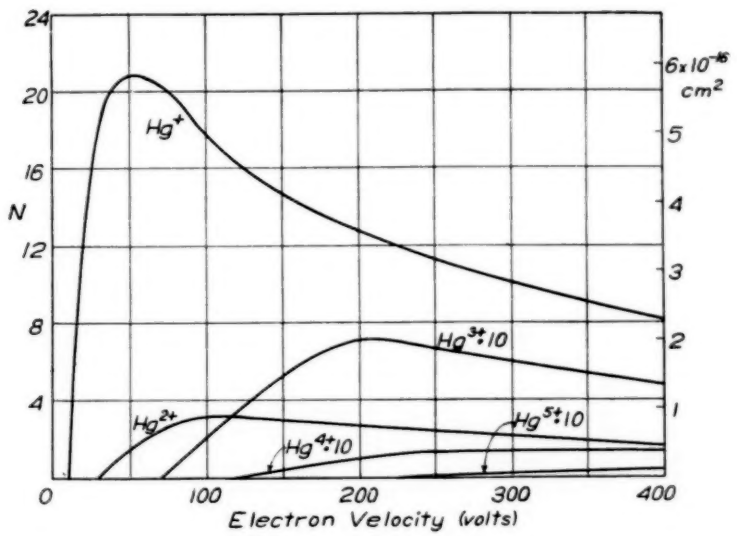

Fig. 9. Number of Hg^+, Hg^{2+}, Hg^{3+}, Hg^{4+}, and Hg^{5+} ions per electron per cm path per mm pressure at 0° C and effective cross-sectional area of the Hg atom.

reduced to 0°C, is from the work of Compton and Van Voorhis.[3] Curve II, corrected to conform to the pressure and temperature data used in this article, is taken from the paper by T. J. Jones.[4] Curve III was obtained by the author and was used in the calculations which follow. Curves II and III agree fairly well as indeed they should since they were obtained by the use of the same type of apparatus. The maximum in the curve found in the present experiment has a magnitude of 25.2 at 75 volts compared to 24.6 at 90 volts as observed by Jones. Beyond the maximum the results of Jones are consistently higher than curve III. At present an attempt is being made in this laboratory with a new apparatus to measure the quantity N^+ with greater accuracy. If such a determination should prove different from the results here given the following results may be easily revised to conform to the new data.

[3] K. T. Compton and C. C. Van Voorhis; Phys. Rev. **26,** 436 (1925) and **27,** 724 (1926).
[4] T. J. Jones, Phys. Rev. **29,** 822 (1927).

Having measured the total number of positive charges and the fraction due to each type of ion it is possible to calculate the actual number of each type by taking values from the curves of Fig. 6, multiplying by the corresponding N^+ from Fig. 8 and dividing by the number of charges on the ion. These results have been plotted in Fig. 9 where N is the number of ions per electron per cm path per mm pressure at 0°C as a function of the electron velocity. The ordinates for the last three ions have been multiplied by 10. Now if the number N be divided by the number of atoms per cc the quotient is the effective cross-sectional area of the Hg atom toward an ionizing collision. This area is indicated by the scale on the right margin of Fig. 9. The kinetic theory value for this area is in the neighborhood of 10×10^{-16} cm^2 depending on one's choice of the recorded values for the diameter of the mercury atom. Although the total positive ion current exhibits a maximum at an electron velocity of about 75 volts yet when the ions are examined separately the maximum yield for Hg^+ occurs at 50 volts. Maxima for Hg^{2+}, Hg^{3+} and Hg^{4+} appear at 115, 210, and 400 volts respectively.

IV. Discussion

Because of its complicated structure there has been no theoretical treatment worked out to predict the ionization potentials in mercury vapor. Of course the first, 10.4 volts, is well known from a host of critical potential experiments. The determination by Lawrence[5] is probably the most accurate, and his value agrees with spectroscopic measurements. Smyth,[6] using a method of positive ray analysis, found doubly charged ions appearing at 19 volts while Carroll,[7] from an analysis of the spectrum of Hg II, gets the same value. These values represent the energy necessary to remove the second electron after the first is gone. If the energy required to remove the first is included they are in satisfactory agreement with the value given by the present investigation.

It was assumed, earlier, that the area under any peak in the e/m analysis curve was proportional to the current due to that type of ion. Suppose the ions are traveling in the x direction and the slit has a width dy. Then for any particular setting of the field E the electrometer measures the number of ions which fall between y and $y+dy$ a quantity which is equivalent to dn/dy where n is the total number of charges between y_0 and y. This is the quantity which is plotted as a function of E, and measuring the area under the curve is equivalent to performing the integration,

$$\int_{E_0}^{E_1}(dn/dy)dE$$

a quantity which has dimensions different from that which we wish to find. The integral which we would like to find is

$$\int_{E_0}^{E_1}(dn/dy)(dy/dE)dE$$

[5] E. O. Lawrence, Phys. Rev. **28,** 947 (1926).
[6] H. D. Smyth, Proc. Roy. Soc. **A102,** 283 (1922).
[7] J. A. Carroll, Phil. Trans. Roy. Soc. **A225,** 365 (1925).

and only in case dy/dE is equal to a constant is the area as measured proportional to the current. The analytical expression for dy/dE can be found from the equations of motion but it is not simple and it involves the unknown initial velocity distributions of the ions. The numerical value therefore can only be roughly approximated. It was thought, therefore, that an experimental attack might prove more fruitful.

Professor Tate pointed out that if the factor by which the area under a peak must be multiplied to get the current is the same for all the peaks then this factor is equal to the total current entering the analyzing chamber divided by the total area under the curve. It was decided, therefore, to measure the current and area at various electron velocities to see if the ratio remained constant when different peaks were involved. The current issuing from the first slit was measured with the high sensitivity galvanometer while the electrometer measured the current through the second slit in the usual way. The experimental error of such a determination is rather large because of the low intensity of the current to the galvanometer. Ten runs were made with electron velocities ranging from 20 to 70 volts. Below 30 volts only the single ion is formed while below 70 volts only single and double ions may exist. In these runs the ratio of current to area showed a maximum deviation of 3 percent from the mean and displayed, moreover, no systematic variation with increasing numbers of doubly charged ions. Tests at higher electron velocities gave similar results although the experimental error was greater. The conclusion is that the area is proportional to the current within the experimental error of this test. It should be pointed out, however, that the experimental error for the determination of the ratio for the second peak alone is perhaps ten or twelve percent since it contains at most only about one fourth of the total area. In general the smaller the peak the less certain are the measurements.

Another test was made by connecting the galvanometer to the plate C Fig. 2, and measuring the current arriving at this plate as a function of the field E. With $E=0$ all the positive ions issuing from the lower slit fell upon C. As E was increased a point was reached at which singly charged ions were prevented from reaching the plate and the remainder was measured by the galvanometer. Here, also, the accuracy is not great because the separation of the ions is not precise at the current densities required, but the results agreed substantially with the previous test.

The original data as represented by the curves in Fig. 4 can be reproduced quite accurately. It is in the interpretation that great care must be exercised lest errors creep in. It is believed that the results as represented by the curves in Figs. 5 and 6 are very close to the true values.

The calculation of the probability of formation of the different types of ions is dependent on the measurements of the total ionization and different observers are somewhat at variance on these values. The results obtained in the present work are in fair agreement with those of Jones, and Compton and Van Voorhis (see Fig. 8) but are not at all in agreement with those of von

Hippel.[8] It is argued by him that a crossed field due to contact potentials swept out the multiply charged ions before they were measured and hence his results apply to Hg^+ only. Even so, the author cannot correlate von Hippel's data with the present work, and it appears that his theory that the maximum yield occurs at twice the ionization potential is untenable.

Smyth,[6] who was the first to investigate the multiply charged ions in mercury vapor by means of a mass spectrograph, states that at the higher velocities the number of doubly charged ions is nearly equal to the number singly charged. From the appearance of his curves it is probable that it is the *current* which is nearly equal in the two cases. If this be true then both Jones and von Hippel have misinterpreted Smyth's data.

It seems to be quite generally assumed that the classical kinetic theory value for the mean free path of an electron is $4(2)^{1/2}$ times the mean free path of an atom of the gas. This value has apparently been used by Hughes and Klein,[9] Compton and Van Voorhis,[3] Jones,[4] and others in their calculations. It seems to the author that this is not the true kinetic theory value for high speed electrons such as were used in all of these experiments, the more appropriate value being

$$\lambda = 1/\pi r^2 N$$

where N is the number of atoms per cc and πr^2 is the kinetic theory value of the cross-sectional area of an atom. The difference in the two points of view is very marked in the case of mercury. The maximum effective cross-sectional area of a mercury atom toward an ionizing collision of the first type calculated on the basis of the latter argument is at least 60 percent of the kinetic theory value, while Jones, and Compton and Van Voorhis on the basis of their calculations get a little over 30 percent for any type of ion. It is interesting to note in the curves of Compton and Van Voorhis that mercury vapor gives the largest yield of positive charges of any gas used and it is among the lowest in probability of being ionized and yet the kinetic theory value for the size of the mercury atom does not differ greatly from the others.

The author has been unable to check the calculations for curve 2, Fig. 3, in the paper by Jones[4] and it is believed that this curve is in error. It also seems that a correction for diffusion due to the large difference in temperature between trap and tube should have been made in the pressure before calculating the values for curve 1 of this same figure.

It is essential to point out that while the number of Hg^+ ions, for instance, has been measured yet what electron was removed in its formation is unknown. This fact makes a theoretical explanation of the observed phenomena even more difficult.

Work on hydrogen and the rare gases has been started and it is hoped that these results may be reported in the near future.

Many thanks are due Professor John T. Tate for his ever present interest and timely suggestions in the prosecution of this problem.

[8] A. v. Hippel, Ann. d. Physik **87,** 1035 (1928).
[9] A. L. Hughes and E. Klein, Phys. Rev. **23,** 450 (1924).

EXPERIMENTS ON THE REPORTED FINE STRUCTURE AND THE WAVE-LENGTH SEPARATION OF THE $K\beta$ DOUBLET IN THE MOLYBDENUM X-RAY SPECTRUM

By Samuel K. Allison and John H. Williams
University of California, Berkeley

(Received November 26, 1929)

Abstract

A nomenclature is suggested for describing the possible positions of the double x-ray spectrometer. A position may be defined by (n_A, n_B) where n_A is the order of reflection on crystal A; n_B the order on B. n_A is to be considered always positive. n_B is negative if the position of crystal B for the reflection of a wave-length incident upon it is such that by turning B through an angle of less than 90° the reflecting surface of B can be made parallel to that of A, and the given wave-length be reflected in this parallel position. If this convention be adopted it is shown that general equations for the instrument may be easily set up. Experiments on the separation of the $K\beta_1$ doublet of molybdenum at the position (2, 2) at 43–46 kv and 22 m.a. show that if the line $K\beta'$ reported by Davis and Purks[1] exists, its intensity is less than 1/10 that of β_1 at these voltages. An average of eight determinations of $\Delta\lambda$ for MoK, $\beta_1\,\beta_2$ gives 0.572 ± 0.003 XU.

Summary of Previous Work

THE doublet character of the $K\beta_1$ line in x-ray spectra has been noted by various experimenters.[1] Allison and Armstrong obtained a considerable separation of the doublet for molybdenum in the 5th order of a single crystal ionization spectrometer, and found $\Delta\lambda = 0.563$ XU. The intensity ratio β_1/β_2 was found to be 2/1. Larsson achieved a separation of the doublet photographically and found $\Delta\lambda = 0.565$ XU. Kellström investigated the doublet in the second order and obtained good separations in palladium and silver, and a very good separation was obtained by Enger and photometered, for the case of rhodium. Davis and Purks, using a double spectrometer, obtained a complete separation of the doublet with both crystals reflecting in the second order. They report a new line $K\beta'$, 0.172 XU. (24 seconds of arc at the dispersion used) to the long wave-length side of $K\beta_1$, and of intensity about 1/3 to 1/2 that of β_1. The voltage at which their tube was operated was not stated in their report. The photographs taken

[1] M. de Broglie, Compt. Rend. **170,** 1053 and 1245 (1920); Duane and Patterson, Bull. Nat. Res. Counc. USA Vol. 1, part 6, p. 393 (1920); Crofutt, Phys. Rev. **24,** 9 (1924); Allison and Armstrong, Phys. Rev. **26,** 701 (1925); Leide, Compt. Rend. **180,** 1203 (1925); Thesis, Lund (1925); Ehrenberg and von Susich, Zeits. f. Physik **42,** 823 (1927); Larsson, Phil. Mag. **3,** 1136 (1927); Kellström, Zeits. f. Physik **41,** 516 (1927); Enger, Zeits. f. Physik **46,** 826 (1928); Stenman, Zeits. f. Physik **48,** 349 (1928); Edlén, Zeits. f. Physik **52,** 364 (1928); Davis and Purks, Proc. Nat. Acad. Sci. **14,** 172 (1928); J. Valasek, Phys. Rev. **34,** 1231 (1929). The same author has also reported, in a paper read at the Dec. 1929 meeting of the Amer. Phys. Soc., that attempts to find the fine-structure lines announced by Davis and Purks were unsuccessful.

by Enger in rhodium were obtained at 50–60 kv and no such line is indicated on them. An attempt has been made to study this new line in molybdenum, using a double x-ray spectrometer.

Apparatus

Several standard molybdenum target tubes supplied by the General Electric Co. for crystal analysis work were used in the course of the experiments. These tubes were cooled by a pump circulating kerosene through the hollow target; the kerosene after entering and leaving the target through insulated glass tubes, was cooled by passing through a copper spiral immersed in running water. The target and the cathode of the tube were at potentials above and below ground respectively. The focal spot was at a distance of 53 cm from crystal A, and the radiation used was taken off at an angle of 8° with the target face. A description of the double spectrometer used has been previously published.[2] The horizontal angular width of the beam (angular width in a plane perpendicular to the axes of rotation of the crystals) was determined by the width of the slits of the instrument, which were 35 cm apart. These slits were 1.5 and 1.8 mm wide in various experiments. The voltmeter which measured the voltage across the x-ray tube was connected between the cathode side of the tube and ground, and therefore measured only half the total potential drop across the tube. It was found by trial that the potential of the anode above ground was very nearly equal to that of the cathode below ground so that the indication of the voltmeter needed only to be multiplied by two. The tube current in all experiments was 22 m.a., the voltage in some was 43 kv and in some 46 kv. In the course of the experiments three different sets of calcite crystals were used.

Nomenclature for the Double X-ray Spectrometer

Since two crystals are used in the double x-ray spectrometer, we have found it convenient to specify their positions by giving two numbers n_A and n_B which represent the orders in which crystals A and B are reflecting respectively. The corresponding glancing angles are θ_A and θ_B. The sign of n_A is to be taken as positive in all cases. The sign of n_B is determined as follows. If the position for crystal B for the reflection of a given wave-length incident upon it is such that by turning B through an angle less than 90° the reflecting surface of B can be made parallel to that of A, and the given wave-length reflected in this parallel position, n_B is negative. If an angle greater than 90° must be traversed in order to bring the crystals to this type of parallel position, n_B is positive. According to this convention, so-called "parallel positions" (Ehrenberg and Mark[3] Case I; Schwarzschild[4] Case II) are special cases of a number of positions in which n_B is to be considered negative. Using this convention, we may write for the dispersion D,

[2] Williams and Allison, J.O.S.A. & R.S.I. **18,** 473 (1929).
[3] Ehrenberg and Mark, Zeits. f. Physik **42,** 807 (1927).
[4] Schwarzschild, Phys. Rev. **32,** 162 (1928).

$$D \equiv \frac{d\theta_B}{d\lambda} = \frac{n_A}{2d \cos \theta_A} + \frac{n_B}{2d \cos \theta_B} \tag{1}$$

in which $d\theta_B$ is the angular range on crystal B corresponding to the wave-length range $d\lambda$, and d is the grating space (assumed to be the same on both crystals).

If the absolute value of n_B is greater than that of n_A and n_B is negative, D is negative, and the sense of rotation of crystal B to pass from shorter to longer wave-lengths is the reverse of that for cases in which D is positive. This is the case, for example, in the position $n_A = 1$, $n_B = -2$, which we designate as the $(1, -2)$ position. Here the dispersion is negative, and for molybdenum K radiation its magnitude is only slightly greater than that from a single crystal reflecting in the first order.

Using the conventions suggested here, Schwarzschild's equation[5] for the "geometric breadth" $\delta\theta_B$, in the case in which the two axes of rotation lie in the reflecting faces of the crystals and are parallel, may be written

$$\delta\theta_B = \tfrac{1}{2} D\lambda\phi^2. \tag{2}$$

In the preceding equation, $\delta\theta_B$ is the angular range through which crystal B may be turned while reflecting the wave-length λ. D is the dispersion defined by (1). ϕ is one-half of the maximum angle between any two rays incident on crystal A in a plane parallel to the axis of rotation of A. In other words, if the only restraint upon the divergence of the x-ray beam is that it must pass through two equal rectangular apertures separated by a distance L, whose height, or dimension in a plane parallel to the axis of rotation of the crystal is h, then $\phi = h/L$.

If the geometric width $\delta\theta_B$ has been made small in comparison to the observed width, and can be neglected, the following equation holds for the width observed for any line in the spectrum at any position of the crystals:

$$W = (W_A^2 + W_B^2 + D^2 W_\lambda^2)^{1/2}. \tag{3}$$

In this equation W represents the half width at half maximum in angular measure of the observed "rocking curve," W_A the half width at half maximum in angular measure of the curve (assumed Gaussian error curve) representing the intensity of reflection from crystal A as a function of the deviations from the Bragg angle, W_B is the analogous quantity for crystal B, D is defined in (1) and W_λ is the half width at half maximum of the line in question in linear measure.

Attempt to Find the Line $K\beta'$

Some of the curves we have taken which have the most direct bearing on the intensity of the line $K\beta'$ are shown in Fig. 1. These curves were all

[5] Schwarzschild expressed this equation in the form $\delta\theta_B = 1/2(\tan\theta_1 \pm \tan\theta_2)\phi^2$ in which the negative sign was to be chosen when the crystals are in a position where "the first incident and the last reflected rays are on opposite sides of the first reflected ray." This agrees with our method of designating the sign of n_B.

taken in the (2, 2) position (both crystals in the second order, reflecting faces not parallel).

Curve (*a*). This curve was taken at 43 kilovolts and 22 milliamperes. The rate of deflection of the electrometer observed on a scale 225 cm from the instrument was 0.744 mm per second at the highest point of $K\beta_1$. At the base-line point on the short wave-length side it was 0.163 mm per second. The voltage sensitivity of the electrometer on the scale at this distance was 4.5 meters per volt. The capacity of the insulated system was not accurately known but was of the order of magnitude of 10^2 cm. The width of the lines

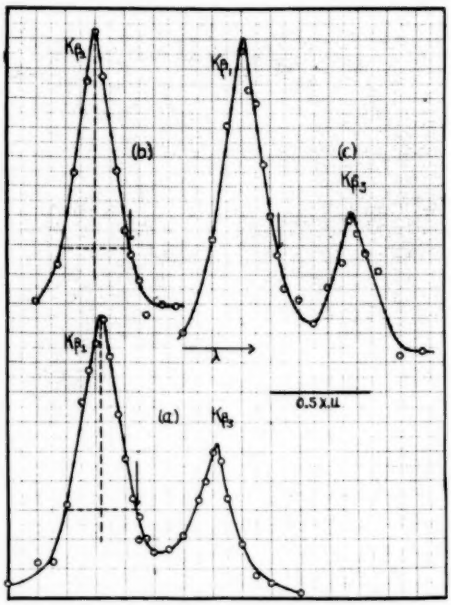

Fig. 1. Typical curves bearing on the intensity of $K\beta'$.

to be expected from geometric sources may be calculated from Eq. (2). The vertical adjustment of the two crystal faces was made by observing the reflection of a beam of light from their faces. This beam as made horizontal by passing through two narrow slits held on a cathetometer and was very nearly perpendicular to the reflecting crystal surfaces. The crystal was then tilted about a horizontal axis until the reflected beam was in the same horizontal plane as the incident beam. This adjustment was accurate to 2 minutes of arc. ϕ was calculated from the height of the focal spot (3 mm) and the height of crystal B (18 mm) and the distance from the target of the tube to crystal B (71 cm). This gives $\phi = 0.0147$, $\delta\theta_B = 9.5$ seconds of arc. The half width at half maximum of the curve for β_1 is approximately 15.5 seconds of arc; the preceding calculation shows that this cannot be explained as due to geometrical causes only. We do not wish to take up the question of the width of x-ray lines here, leaving this for a later publication. The half

width at half maximum of the curve at (1, −1) for these crystals was 3.1 seconds of arc.

Curve (*b*). This curve was taken with the same arrangement as that of curve (a) except that a vertical stop 7.5 mm high was introduced at a distance of 48 cm from the target. This gives $\delta\theta_B = 5.2$ seconds of arc from Eq. (2). The voltage was 43 kv. The rate of deflection of the electrometer (scale and sensitivity as for curve (a)) at the highest point on the peak was 0.398 mm per second; at the lowest point shown on the short wave-length side it was 0.093 mm per second. The half width of the peak at half maximum is about 14 seconds. An accident to the x-ray tube prevented continuing the curve to cover β_3.

Curve (*c*). This curve was taken on a different set of crystals and with a different target from that used in curves (a) and (b). The voltage was 46 kv. The rate of deflection of the electrometer (same arrangement as for (a) and (b)) at the highest point of β_1 was 0.475 mm per second; at the lowest point on the short wave-length it was 0.162 mm per second. The value of ϕ and consequently of $\delta\theta_B$ was the same as that for curve (a). For various unknown reasons the curve (c) is less reliable (as indicated by the scattering of the points) than curves (a) and (b). The half width at half maximum of the curve at (2, −2) for the crystals used was 1.5 seconds of arc.

The vertical arrows in Fig. 1 show the angular positions at which β' should appear (24 seconds of arc to the long wave-length side of β_1) according to the results of Davis and Purks.[1] In curves (a) and (b) the total intensity here is about 1/5 of that at the maximum. In these curves, the vertical dotted line represents the center of the line $K\beta_1$; the horizontal dotted line its width at an angular distance of 24″ from the center. It is evident that within the accuracy of the readings the curve is symmetrical in this region about an ordinate through its maximum. We can therefore obtain no positive evidence for the presence of the line $K\beta'$ at the voltage used.

A rough estimate of the maximum possible intensity in the form of the line $K\beta'$ which could be present in our curves may be obtained by assuming a Gaussian error curve for β' symmetrical about the position indicated, and of the same half width as that for β_1. The distortion of the symmetry of β_1 which would be thus produced can be plotted by adding up the contributions from β_1 and the supposed β' at various abscissae. Proceeding by this method the conclusion was reached that the curves (a) and (b) could not have failed to show evidence of a line in the specified position of intensity 1/10 that of β_1. Our conclusion is therefore that there is no line at this position of intensity greater than 1/10 that of β_1 under the conditions of the experiment.

Determination of the Wave-Length Separation of the Doublet $K\beta_1$, β_3 in Molybdenum

In the course of the investigation many curves have been taken of the doublet in question in various positions of the double spectrometer. Eight of the most reliable of these have been selected for the purpose of obtaining an accurate value of $\Delta\lambda$ for this doublet. The results are shown in Table I.

TABLE I. *Observations on the wave-length separation of* β_1, β_2.

Position n_A	Position n_B	Dispersion from Eq. (1)	$d\theta_B$ obs.	Av. $d\theta_B$	$\Delta\lambda$ calc.	Weight
1	1	68.46″/XU	39.1″	39.1″	0.5711XU	2
1	2	103.8	61.0 61.2 59.5	60.6	.5835	9
1	3	140.7	80.0	80.0	.5687	4
2	2	139.2	78.5 77.0	77.8	.5587	8
2	3	176.0	101.5	101.5	.5766	5

The weights assigned in the last column of Table I are the products of the number of observations for a given position by (n_A+n_B) for that position, since it was supposed that higher dispersion gave more accurate results. The weighted mean of the measurements shown in Table I is

$$\Delta\lambda=0.572\pm0.003\text{XU}$$

in which the probable error has been computed according to the usual methods.[6] This value is slightly higher than the values 0.563 XU observed by Allison and Armstrong[1] and 0.565 XU observed by Larsson.[1] In general the effect of greater resolution of a close doublet should be to increase the estimate of its wave-length separation. The errors in the value quoted must be mainly due to two factors (1) the uncertainty of the electrometer readings, and (2) the fact that a change of temperature of the crystals might have taken place between the time of reading one peak and the time for the next.

[6] For instance, Birge, Phys. Rev. Supp. **1**, 1 (1929), pp. 5–6.

THE INTENSITY MAXIMA IN THE CONTINUOUS HELIUM SPECTRUM

By Jane M. Dewey
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(Received December 9, 1929)

Abstract

The position of the maxima of the continuous spectrum of helium was measured with an arc in which measurements of ion concentration was made. The displacement of the maxima to the red by stray fields in the gas was calculated from the formula $E=-2e(eF)^{1/2}$ given by Robertson and Dewey and more recently by Kudar. The observed displacement is always larger than the calculated. Reasons for this are discussed.

IN A paper in this journal[1] H. P. Robertson and the author suggested an explanation of the displacement of the maxima of continuous atomic spectra to the red of the limit of the spectral series. It was assumed that the effect is due to the stray fields set up in the gas by the ions and free electrons, and the least energy for which aperiodic orbits are possible was calculated from the complete formula for the Stark effect on the basis of the classical quantum theory. Kudar[2] has recently obtained the same value for this limit of the continuous spectrum from general reasoning on the basis of the quantum mechanics. It is not possible to carry through the calculation in quantum mechanics as the complete equation is not soluble and is known to give no discrete states unless some restriction is imposed. Since the quantum mechanics must go over into ordinary mechanics for large quantum numbers, or atomic states of energy close to zero, the classical mechanics should give the correct formula for the displacement of the spectral limit. The uncertainty which it introduces lies rather in the fact that it gives no information as to the relative probabilities of the various transitions which are possible.

Experimental Procedure

The spectrum of a hot cathode helium arc very similar to that described in an earlier paper[3] was photographed, with a Hilger E3 quartz spectrograph, and the position of the maximum intensity in the continuous spectra determined with a recording microphotometer. The cathode of the arc was a cylinder of platinum foil, coated with barium oxide and heated by a current put through it lengthwise. A Langmuir exploring electrode used to measure the electron concentration was placed in the center of the cylinder with its axis perpendicular to the axis of the cylinder. One photograph on which the intensity of the continuous spectra could be measured was obtained with a

[1] Robertson and Dewey, Phys. Rev. **31**, 973 (1928).
[2] Kudar, Zeits. f. Physik **57**, 705 (1929).
[3] Dewey, Phys. Rev. **32**, 918 (1928).

Schüler tube containing a similar electrode. Even when the exploring electrode was small (1 mm of seven mil wire) the discharge tended to avoid its neighborhood, as could be seen by visual observation of the tube. This was probably due to recombination of the ions on the glass insulation of the electrode and to the cooling effect of the electrode. As the curves from which the electron temperatures and concentrations were obtained were regular and obtained without difficulty, the removal of electrons by the electrode itself cannot have caused a serious disturbance. The most serious difficulty in the measurement of ion concentration was that it sometimes caused a sudden increase in the current which melted the glass insulation from the electrode. The ion concentration which could be obtained in the tube was limited by the heating effect.

Helium was chosen rather than an alkali metal to avoid the possibility of the atomic spectrum being complicated by unresolved bands or continuous molecular spectra. The helium recombination spectra have been observed by Paschen[4] and more recently by Mohler and Boeckner.[5] For purposes of photometric measurement they have the serious disadvantage of being accompanied by bands. Mohler and Boeckner report that the bands are greatly reduced in intensity by the addition of a trace of mercury to the helium but in the discharges used in this investigation this did not appear to be the case. It was not found possible to eliminate the bands in any way except by the reduction of both pressure and ion concentration, which also reduced the intensity of the recombination spectra. The arc was more suitable than the Schüler tube as the bands were strong only when a high current was put through the arc. The tube used by Mohler[6] and by Mohler and Boeckner apparently would give better spectra but has the disadvantage that the ion concentration must be measured by an indirect method. Probably the bands were weakened on the one plate taken with a Schüler tube on which the intensity of the continuous spectra could be measured by some impurity accidentally present. This was the first plate taken with a newly set up Schüler tube and all subsequent exposures showed very strong bands. The difficulty of estimating the intensity of the continuous spectrum when bands appear on the plate can be seen on the excellent reproductions which accompany Paschen's paper. The bands are strongest in the neighborhood of the $2p$ limit but the weak bands in the ultra-violet also make measurements on the $2s$ limit difficult. The small dispersion of the spectrograph used made measurements at the $2p$ limit of parhelium impossible. The range of ion concentrations included in these results is small and the estimated fields uncertain but, as it was necessary to discontinue the investigation, it seemed worthwhile reporting such results as were obtained.

Table I gives the results. The field is calculated from the formula of Holtsmark,[7] taking account of the presence of both ions and electrons by doubling

[4] Paschen, Berl. Sitzb. Math. Phys. K. 1926, p. 135.

[5] Mohler and Boeckner, Bureau of Standards Jour. of Research **2**, 489 (1929).

[6] Mohler, Phys. Rev. **31**, 187 (1928).

[7] Holtsmark, Ann. d. Physik **58**, 577 (1919), Phys. Zeits. **20**, 162 (1919) and **25**, 73 (1926). The formula used is $F=3.9n^{2/3}e$. This gives the most probable field. The mean field is somewhat larger.

the electron concentration. This probably gives too small a field. Under "displacement of maximum" the distance in cm^{-1} of the maximum intensity of the continuous spectrum from the limit of the spectral series for zero field

TABLE I

Series limit	Electron concentration	Calculated field (e.s.u. per cm)	Displacement of maximum observed	calculated
$2p$	3.6×10^{12}	0.69	160 cm^{-1}	91 cm^{-1}
$2s$	3.6×10^{12}	0.69	140	91
$2p$	5.1×10^{12}	0.87	175	105
$2s$	9.1×10^{12}	1.3	185	125
$2s$	1.1×10^{13}*	1.4	205	130

* Schüler tube.

is given. From the formula $E=-2e(eF)^{1/2}$ the calculated displacement is obtained, where F is the field and e the charge on the electron.

DISCUSSION

The displacement of the limit observed is in every case larger than that calculated. This is to be expected from the serious error in the electron concentrations introduced by the avoidance of the neighborhood of the exploring electrode by the discharge. Since the intensity of the continuous spectrum increases as the square of the electron concentration the spectrum observed will be essentially the spectrum of the region of the discharge in which the concentration is highest. All other sources of error, both in measurement and in calculation, will probably result in discrepancies in the same direction, but it is probable that this error is so large as to mask all others. One source of error in the calculation may be large. Oppenheimer[8] has pointed out that there is a possibility of dissociation, and therefore of recombination on the basis of the new mechanics even when the energies of the ions and electrons do not permit it according to classical mechanics. The general argument that the results of the two types of mechanics must approach each other for large quantum number makes it improbable that this introduces serious error, although it is conceivable that it might. It is not possible to estimate the magnitude of the effect from Oppenheimer's or Kudar's formulae as for the upper excited states of the atom the change in energy due to the field is as large as the total energy of the states even for small fields and cannot be calculated from perturbation theory.

A more complete study of the effect would be desirable, accompanied if possible by a determination of the field in the source by an independent method, such as the intensity of forbidden lines appearing in its spectrum, as it appears to give a reasonably direct method of estimating the ion concentrations in stellar sources.

These measurements were made in Palmer Physical Laboratory, Princeton University, while the author was a fellow of the National Research Council. She is greatly indebted to Dr. K. T. Compton for his interest in the work as well as for extending to her the privilege of working in the laboratory.

[8] Oppenheimer, Phys. Rev. **31**, 66 (1928).

SCHOTTKY EFFECT AND CONTACT POTENTIAL MEASUREMENTS ON THORIATED TUNGSTEN FILAMENTS

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(Received December 7, 1929)

Abstract

The Schottky effect for thoriated tungsten filaments is investigated and Schottky's relation that $\log i \propto (V)^{1/2}$ is verified at high fields, but fails at gradients below 10000 volts/cm, even for fully activated surfaces. This lack of saturation at low fields is accentuated by the effect of bombardment with high velocity positive ions, such bombardment apparently producing a surface roughening and consequently increased fields in local areas. Investigation with low accelerating and retarding voltages, while varying the temperature and state of activation of the filament, allows a comparison of the contact potential and the work function at the absolute zero of temperature (ϕ_0) for the thoriated surface. The two values (contact potential and ϕ_0) are found to vary with a one-to-one correspondence if ϕ, the work function at the temperature of measurement, be allowed a temperature coefficient. This coefficient is much larger than can be attributed to the specific heat of the electrons in the metal. The electrons with high velocities show a Maxwellian velocity distribution. Near the zero of potential there are certain anomalous effects and a "patch surface" is postulated which, in a qualitative manner, explains this behavior and the lack of current saturation with voltage gradients below a limiting value.

SCHOTTKY,[1] many years ago, derived an equation to explain the increase of saturation thermionic current with anode voltage. This relation has been verified by many investigators for pure metallic electron emitters, especially in the last few years. With one or two exceptions, the analogous effect with composite cathodes has been neglected, and the present paper deals with the current-voltage relations for thoriated tungsten filaments over a range of anode potentials from retarding potentials of 10 volts to accelerating potentials of 5000 volts, corresponding to potential gradients of nearly 500000 volts/cm.

A number of tubes were used in these experiments, varying slightly in detail but of the same general design. A 1.6 mil thoriated tungsten filament was stretched in the center of a cylindrical nickel or molybdenum anode. This was constructed in three pieces, on the guard ring principle. An alkaline earth metal was vaporized on the wall of the tube as a getter. The tube was given the best possible exhaust, baked, the metal parts degassed, and then sealed off from the pumping system. The tube was so designed that it could be completely immersed in liquid air.

The temperature of the filament was determined from the watts input according to the latest temperature scale of Jones.[2] Since all three parts of the

[1] W. Schottky, Phys. Zeits. **15**, 872 (1914); also Zeit. f. Physik **14**, 63 (1923).
[2] H. A. Jones, Phys. Rev. **28**, 202 (1926).

anode were maintained at the same potential but currents were measured only to the center cylinder, the effects of filament cooling at the leads and of field distortion at the edges were eliminated. Currents were measured by galvanometers and a Rawson multimeter, with a system of shunts giving a measuring range from 1 ampere to 5×10^{-11} amperes. Batteries, a 1500 volt dc generator and a 20000 volt full wave rectifier gave a complete range of anode potentials.

Langmuir and others[3] have described the methods of manipulation of thoriated tungsten cathodes. In these experiments the state of activation of the filament was controlled by allowing thorium to diffuse to the surface at lower temperatures, or by raising the temperature and removing it by evaporation. It is practically impossible to obtain a completely deactivated thoriated filament even by flashing at very high temperatures since diffusion occurs while the filament is cooling. In the present instance it was possible to obtain values of θ as low as 0.30 (θ = fraction of the surface covered).

Becker[4] has distinguished between the amount of barium present on a tungsten filament and the amount effective in lowering the work function. Since in the experiments reported in the present paper the emission obtained from the filament was used as the criterion of θ according to Langmuir's relation that $\log i \propto \theta$, there is no contradiction and θ might more properly be defined as the fraction of the tungsten covered with thorium atoms which are effective in lowering the work function.

Becker and Mueller[5] reported that partially activated thoriated and caesiated tungsten surfaces obeyed Schottky's relation,

$$\log i = \log i_0 + \frac{K}{T}\left(\frac{dV}{dx}\right)^{1/2}$$

at high electric fields, but deviated from this as zero potential was approached. They discussed the nature of the fields to be expected close to non-homogeneous surfaces and concluded that poor saturation was to be expected from partially activated cathodes. This effect has been known for some time, but as a subject of detailed study it has been neglected. Dushman[6] and others in their calculations of the electron emission from composite surfaces have projected the $\log i$ vs. $(F)^{1/2}$ line from high fields to zero potential and assumed this as the current emitted at zero field. Since this extrapolated value was several times greater than the current actually obtained, some doubt was thrown on the procedure and it was thought important to investigate in detail the relation between electron current and anode voltage so as to obtain some sort of an explanation of the departures at low fields and perhaps a work-

[3] I. Langmuir, Phys. Rev. **22,** 357 (1923); S. Dushman and J. Ewald, Phys. Rev. **29,** 857 (1927).

[4] J. Becker, Phys. Rev. **33,** 1082 (A) (1929).

[5] J. Becker and D. Mueller, Phys. Rev. **31,** 431 (1928).

[6] Dushman and Ewald, Reference 3; K. Kingdon, Phys. Rev. **24,** 510 (1924); Dushman, Dennison and Reynolds, Phys. Rev. **29,** 903 (1927).

ing picture of the surface. The procedure and results will be briefly stated, and the theory and conclusions left for consideration at the end of the paper.

Figure *i* shows two typical curves obtained at the same temperature with two values of θ, $\theta_A > \theta_B$. It will be observed that above V_1 both curves follow

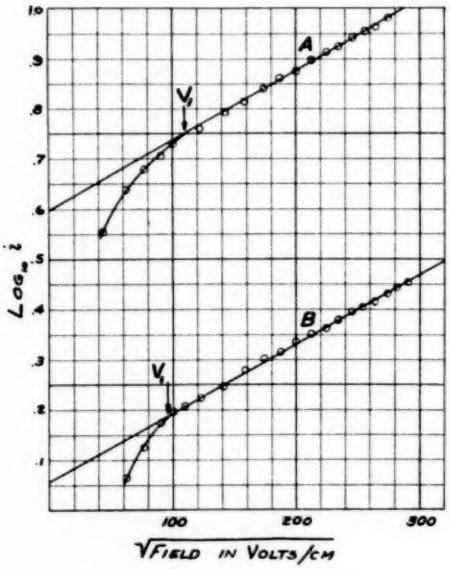

Fig. 1. Typical curves, for two partially activated thoriated filaments, $\theta_A > \theta_B$.

straight lines of approximately the same slope. The theoretical slope can be calculated from the field gradient at the filament surface, as derived from the tube dimensions. The observed slopes varied somewhat, running on the aver-

TABLE I. *From tube geometry,* $T[\Delta \log i/\Delta(V)^{1/2}] = 18.4$.

Run	Temp.	θ	$[\Delta \log i/\Delta(V)^{1/2}]$	$T[\Delta \log i/\Delta(V)^{1/2}]$
28	1045°K	1.0	0.0189	19.77
27	1101	1.0	.0184	20.40
26	1295	1.0	.0138	17.90
87	1350	1.0	.0141	19.05
88	1350	1.0	.0148	19.95
91	1350	0.5	.0150	20.25
101	1350	1.0	.0146	19.70
102	1350	1.0	.0150	20.25
116	1350	0.9	.0143	19.30
107	1375	0.9	.0136	18.70
108	1375	0.9	.0142	19.52
92	1450	0.8	.0145	21.02
112	1450	1.0	.0141	20.45
114	1450	0.9	.0165	23.90
32	1500	0.6	.0127	19.06
			Average	19.93

age about 10 percent higher than the calculated. Table I gives results for various runs at different temperatures and values of θ.

The position of the critical field V_1 must next be considered. This varied slightly from run to run, and the discussion of the effect of positive ion bombardment will show one reason for this variation. However, under the best vacuum conditions, the point of departure from the straight line was constant at about 10000 volts/cm. This appeared to be a limiting minimum value, independent of the temperature and of the state of activation of the filament. So, between $\theta = 0.30$ and $\theta = 1.0$, and between $T = 1100°\text{K}$ and $T = 1600°\text{K}$, Schottky's relation held with very fair accuracy for fields greater than 10000 volts/cm, and this limiting value was characteristic only of the surface thorium on tungsten.

It is interesting to note that in Becker and Mueller's paper, Fig. 5 shows the curve approximating to a Schottky straight line at high voltages but departing from it at about 15000 volts/cm, which is in fair agreement with the results obtained here.

The portion of the curves between V_1 and V_0, the zero of applied potential, presents something of a puzzle. The results vary a great deal, but averaging a large number of runs and eliminating possible complicating factors, there seems to be a certain amount of regularity. Curves *A* and *B* of Fig. 1 illustrate this. It will be noted that curve *A* approaches the dotted straight line more gradually than does curve *B*. These are two runs at the same temperature, where $\theta_A > \theta_B$. This example and numerous others lead to the generalization that the point of departure, V_1, is approximately independent of θ, but as θ is decreased, the curve falls away more and more steeply. So far, attempts exactly to analyze this portion of the data have failed, yielding only this observed qualitative result.

Removal of liquid air from around the tube resulted in the liberation of small amounts of gas. Thoriated tungsten surfaces are very sensitive indicators of the presence of the least traces of even chemically inert gases, since positive ions produced by electron impacts are accelerated to the filament and remove thorium, reducing θ and consequently the emission obtainable at a given temperature. With "residual gas" ions, this effect becomes important at around 40–50 volts. After such *low voltage bombardment*, the general nature of the log i vs. $(V)^{1/2}$ curves was unchanged, but was shifted vertically downward due to the decrease in the emission current. However, if *bombardment at 400 volts or higher* was maintained for a considerable period of time (15-60 minutes), subsequent log i vs. $(V)^{1/2}$ curves in good vacuum exhibited marked changes.

Figure 2 illustrates this. Curve *A* is a normally activated filament. Curve *B* was taken after positive ion bombardment at 400 volts. The filament was then flashed at 2800°K and reactivated and curve *C* taken. This last has been shifted downward in the figure for purposes of spacing. Actually the upper parts of *B* and *C* practically coincide, while at low voltages the currents of *C* are considerably higher than those of *B*.

The effect of bombardment was a semi-permanent one. Subsequent activation and deactivation by temperature (below 2700°) shifted the curve along the current axis but did not otherwise alter its unique character. Flashing at

2700°K or higher, where rapid sintering of tungsten is known to take place, destroyed the effect of bombardment and subsequent activation produced normal log i vs. $(V)^{1/2}$ curves.

When gas was present in the tube and a run was made, first with ascending and then descending voltages, bombardment occurred while readings were being taken and the curve would not retrace its original path. When the maximum potential used was 1000 volts or higher, the return curve was actually higher than the ascending one, but broke away sooner and crossed the first. A second ascending curve retraced the previous descending one, returning still higher and giving a second sort of hysteresis loop. Thus a filament which at low fields gave higher emission currents than a bombarded one which

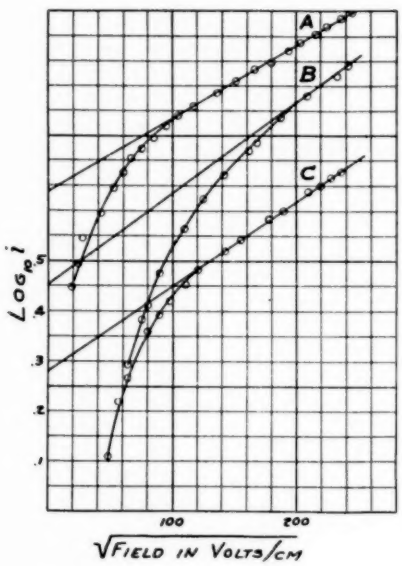

Fig. 2. Curves illustrating effect of positive ion bombardment at 400 volts. Curve A, normally activated filament; B, after bombardment; C, after reactivation. Curve C is shifted downward from practical coincidence with A.

had less thorium present, actually produced less current than the bombarded filament when fields of the order of hundreds of thousands of volts per centimeter were applied. The indication was that something other than the amount of thorium present determined the emission.

A study of the diffusion characteristics of the bombarded filament throws some light on this behavior. Subsequent to severe bombardment, diffusion of thorium to the surface of the wire from the interior occurred at temperatures much lower than in normal thoriated tungsten filaments. The activation rate at 1800°K was about that expected in a normal wire at 2100°K. It is known that diffusion of thorium in tungsten occurs most readily in fine grain structures, presumably along the crystal boundaries. An explanation suggests itself, that the effect of the bombarding positive ions may have been to rup-

ture the surface of the tungsten, producing a superficial fine crystal structure which facilitated the diffusion of thorium atoms. If this had also produced some sub-microscopic roughening, there would have been points where the field strength would have been greatly increased. This would account for a more rapid increase of the current with applied voltage, and an apparent, but not an actual deviation from Schottky's relation.

It was not possible during the course of this investigation to repeat these experiments with a pure tungsten filament and verify this hypothesis, free from the complicating influence of the thorium. However, Bartlett[7] has reported similar results with pure tungsten, giving curves resembling those shown here. He reported difficulty in eliminating gas, and stated that his procedure was to flash the filament and then bombard his anode to red heat to remove gas. Only after this process was he able to obtain satisfactory results. He had only 1000 volts available and was able to go only to about 60000 volts/cm. Up to this point his curves were steeper than the theoretical Schottky line, but were rounding over and approaching this slope. His degassing schedule was an ideal one to produce positive ion bombardment of his filament. It seems possible that the lack of saturation he reports may be the same phenomenon noted here—a roughening of the surface by a positive ion "sand blast"—and that if he had continued to higher fields the curves might have straightened out along the conventional Schottky line. The highest fields used by Bartlett are of about the same order of magnitude as the point of departure of the bombarded curves in the present investigation.

II. Low and Retarding Potentials

If the electrons emitted from a filament at a given temperature all had zero or a constant initial velocity normal to the emitting surface, at a certain anode potential the current should rise abruptly from zero to its full value, and then remain constant, subject to the increase predicted by Schottky's equation, as the potential is increased. It has been shown by several investigators[8] that the emitted electrons have an initial velocity distribution given by Maxwell's equation (via Schottky)

$$i = i_0 \frac{2}{\pi^{1/2}} \left[\left(\frac{Ve}{KT} \right)^{1/2} \epsilon^{-Ve/KT} + \int_{(Ve/KT)^{1/2}}^{\infty} \epsilon^{-x^2} dx \right].$$

Thus, if complicating effects such as voltage drop along the cathode be eliminated, the current should break at a definite potential, and as the anode is made more negative the current should fall away so as to make the log i vs V plot substantially a straight line. The sharp break point defines the absolute zero of potential, i.e., the state at which the anode and cathode are at the same potential, and the difference of this from the zero of applied voltage gives the contact difference of potential (CDP) between the anode and cathode materials. Comparison of two different cathodes or states of surface of the

[7] R. S. Bartlett, Proc. Roy. Soc. **A121,**, 456 (1928).

[8] Davisson and Germer, Phys. Rev. **24,** 666 (1924); Germer, Phys. Rev. **25,** 795 (1925).

cathode with the same anode provides a method of determining changes in the contact potential of a material.

This method was used in examining thoriated tungsten filaments with accelerating and retarding fields in the neighborhood of zero field. Figure 3 shows a typical curve. It will be noted that the left hand portion of the curve follows a straight line, and that after passing through the transition region near zero, the points again approach the nearly straight line saturation value. It was decided to consider the intersection of these two lines, as the experimentally determined zero of potential as a basis for the determination of contact potential differences. This is designated in Fig. 3 as V_c. A justification of this will be given in the discussion to follow.

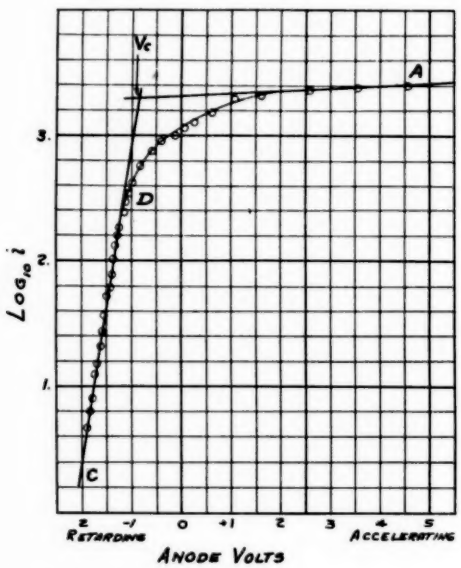

Fig. 3. Typical curve for determining contact potentials.

That part of the straight line just to the left of V_c is a theoretical, not an experimentally obtained curve, since the plotted curve falls away from it before V_c is reached. One cause of this deviation is the voltage drop along the filament cathode. The length of the center anode cylinder of the tube was 2.8 cm, and the difference in the cathode potential opposite the upper and lower ends was considerable and varied with the filament temperature. For this, a first order correction was applied. This was accomplished by first determining the potential of the mid-point of the filament. Then since the current from the most negative end was greater than from the most positive end, and the contribution of each element of the filament did not vary linearly along the filament, a method of graphical integration was used to determine what may be designated as the potential of the effective mid-point of the filament. This is the potential, which applied to a unipotential cathode would give the same observed current. The correction showed that only a part of the devia-

tion near zero could be attributed to the effect of filament drop since, whereas the correction was effective over only a few tenths of a volt range, the observed deviation extended over a range of one or more volts on either side of the determined zero. The effect of the correction on the retarded straight portion of the curve was simply to produce a small lateral shift, altering the actual value of the contact potential break but not the slope of the $(\log i)/V$ line.

Taking this corrected point as zero, and calculating from the filament temperature the fraction of the corresponding saturation current having different initial velocites, a series of points was obtained from Maxwell's distribution law coinciding with the corrected experimental line within the limits of experimental error. Over a 500°C temperature range this effect was verified. At least those electrons with high initial velocities had a Maxwellian velocity distribution. It will be shown later that the apparent deviation of the low velocity electrons (those contributing to the curve near zero voltage) from this distribution was not an actual deviation but was the result of quite another phenomenon.

The low electronic work function of a composite surface, such as thorium on tungsten, has generally been attributed to the effect of the contact difference of potential existing between the thorium and tungsten atoms at their point of contact.[9] Whether the electrons come from the tungsten and are aided in their escape by local fields due to the thorium film, or whether they come from the thorium atoms themselves, it is impossible to state with certainty. Since the currents obtained from the thoriated tungsten are slightly greater than those from a pure thorium filament at the same temperature, and some tens of thousands of times greater than from pure tungsten, it seems reasonable to assume that the emission is that from thorium, modified by the proximity of the tungsten base.

Dushman's[10] derivation of the thermionic emission equation leads to the result:

$$i_0 = A T^2 \epsilon^{-b_0/T}$$

where $b_0 = (e\phi_0/K)$, or $\phi_0 = (K/eb_0)$, and ϕ_0 is the work function of the surface at the abolute zero of temperature. From this equation, it is seen that the value of ϕ_0 for any condition of cathode surface can be found from the slope of the line obtained by plotting $(\log i - 2 \log T)$ against $1/T$. This value of ϕ_0 varies with the amount of thorium present on the surface, ranging from 4.5 volts ($b_0 = 52400$) for pure tungsten, to 2.6 volts ($b_0 = 30500$) for a completely activated filament.

In a preceding paragraph it was pointed out that the difference of the abscissa coordinate V_c from the zero of applied potential V_0 gave a measure of the contact difference of potential between cathode and anode materials. By measuring this difference for different values of θ, to each of which corresponded a definite value of ϕ_0 obtained as just described, a relation was arrived

[9] O. W. Richardson, Phil. Mag. **43**, 557 (1922).
[10] Dushman, Phys. Rev. **21**, 623 (1923).

at connecting the change in contact potential with the change in ϕ_0 for a range of surface conditions. Measurements of the C.D.P. were also made over as wide a range of temperatures as the measuring instruments and other limiting conditions allowed. Since the C.D.P. should be related to ϕ, the work function at the temperature of measurement, while ϕ_0 should be a constant independent of temperature, and presumably

$$\phi = \phi_0 + \pi(T),$$

a study of the change of the C.D.P. with temperature should give an insight into the nature of the function $\pi(T)$. Results are tabulated in Table II.

TABLE II. *Results showing variation of ϕ with temperature.*

I	II	III	IV	V	VI	VII	VIII
Run	Temp.	ϕ_ϕ	Observed π_θ	π_1	Corrected π_θ	Deviation (IV–VI)	Deviation %(IV–VI)
57	1175°K	2.85 v	(−)0.3 v	0.08 v	0.30 v	0	0
73	1175	2.73	.4	.30	.18	−.22	—
75	1175	2.68	.3	.28	.10	−.20	—
78	1295	2.68	.3	.28	.36	−.06	16.7
66	1320	3.14	.9	.39	.90	0	0
56	1350	2.85	.5	.28	.68	−.18	26.5
61	1350	2.74	.6	.49	.57	−.03	5.3
59	1350	3.18	1.1	.55	1.01	−.09	8.9
76	1350	2.66	.6	.57	.49	−.11	22.5
84	1375	3.60	1.4	.43	1.48	−.08	5.4
86	1400	2.70	.6	.53	.64	−.04	6.2
63	1450	3.58	1.6	.65	1.62	−.02	1.2
83	1475	3.60	1.7	.73	1.70	0	0
72	1500	2.84	1.1	.89	.99	−.11	11.1
77	1500	2.65	.7	.68	.80	−.10	12.5
68	1550	3.79	2.1	.94	2.05	−.05	2.4
82	1575	3.60	2.0	1.03	1.91	−.09	4.7
64	1660	3.58	1.9	.95	2.07	−.12	5.8
70	1755	3.79	2.4	1.24	2.48	−.08	3.2
						Average	−7.8%

Column III gives the value of ϕ_0 for different values of θ as obtained from the emission data. Column IV lists the contact potential differences from the measurements with retarding fields. These are denoted by π_θ, since they represent results for varying values of θ. Let ϕ_1 denote the value of ϕ_0 for $\theta = 1$ and ϕ_θ for any given value of θ; π_1 and π_θ the corresponding C.D.P. values. Then it is assumed that $\Delta\pi_\theta = \pi_\theta - \pi_1 = \Delta\phi_\theta = \phi_\theta - \phi_1$. Hence $\pi_1 = \pi_\theta - \Delta\phi_\theta$.

Thus, from the observed values of π_θ, an averaged plot of π_1 was obtained as a function of the temperature. These values of π_1 are given in column V. This smoothed curve was used to give corrected values of π_θ, from the observed $\Delta\phi_\theta$. Column VI shows these corrected results, for comparison with the originally observed values of C.D.P. (π_θ). The best justification for this process is the agreement between columns IV and VI. The last two columns give the actual and percentage deviations of IV and VI. In VIII, those cases have been omitted for which the values of $(\pi_\theta - \Delta\phi_\theta)$ were of the order of magnitude of the probable errors of measurement.

In most cases in the experiments, the measurements with retarding fields were made at 0.05 volt intervals throughout the critical range. However, due to the approximation in the correction for filament drop, no claim is made to an accuracy of better than 0.1 volt. The actual magnitude of the measured C.D.P. between the filament and nickel anode can have very little significance. The nickel was at all times positive to the filament. It was noted that after long operation it was impossible to reproduce the earlier readings, an effect traceable to evaporation of thorium to the anode and a consequent shift in the potential of the nickel surface.

The foregoing calculations were based on the assumption that $\Delta\phi_\theta = \Delta\pi_\theta$, and the reasonably close agreement resulting seems to justify this assumption. This seems to be a direct experimental support of Richardson's theory of the essential identity of contact difference of potential and difference of work functions. From this viewpoint, the data of column V are of considerable qualitative interest. They may be interpreted as giving the temperature coefficient of ϕ.

Previous investigators have failed to show conclusively that the work function changes with the temperature. Germer[11] obtained what appeared to be evidence for such a change, but later attributed it to temperature effects inherent in the anode. Whatever the effect in pure metals—tungsten, platinum, and the like—it is small, and the conclusion reached is that the electrons which produce the thermionic current do not share in the temperaure equilibrium in the metal. If they did have a share in the specific heat of the solid they should, by the equipartition theory, contribute an amount at most of the order of $2kT$, an effect barely detectable in these experiments. The results obtained here indicate a temperature coefficient of ϕ of the order of 2×10^{-3} volts per degree, or in the neighborhood of $20kT$. To attribute this to degrees of freedom is obviously absurd.

The constancy of ϕ_0 in the emission equation is not to be doubted, and the method by which the work function is here determined precludes obtaining the value of ϕ and analyzing it for temperature dependence. DuBridge[12] has pointed out that since, for composite surfaces, A in the equation is not constant, and ϕ_0 is by definition a constant, any temperature coefficient of ϕ will be concealed in A. No effort has been made as yet to study the mutual dependence of A and ϕ in a quantitative way.

III. Theoretical Treatment

Langmuir and also Richardson and Young[13] have considered a patch surface to account for lack of saturation of electronic and photoelectric currents fom thin electropositive films. Becker and Mueller[14], in their paper on thoriated and caesiated filaments, calculated that at non-homogeneous surfaces the fields between the two types of atoms should produce the observed depar-

[11] Germer, Reference 8.

[12] DuBridge, Proc. Nat. Acad. Sci. **14,** 788 (1928).

[13] Langmuir, General Electric Rev. 504 (1920); Young, Proc. Roy. Soc. **A104,** 611 (1923).

[14] Becker and Mueller, Reference 5.

tures from Schottky's plot at low applied fields. While any concrete representation of phenomena of atomic behavior may be questioned, the following considerations apparently do offer a tentative explanation of the effects set forth in the foregoing sections of this paper. These considerations were suggested by Dr. K. T. Compton in discussing the interpretation of the present work. It was learned later that the same idea had been carried to a partial quantitative stage a number of years ago by Langmuir and Mott-Smith, but not published.

The work function of a surface is the work required to remove an electron from the surface to infinity. The Thomson method of images furnishes a way of calculating this work, which can be expressed to a first approximation as

$$\phi = -\int_0^\infty (e^2/4x^2)dx.$$

But this leads to an infinite value for ϕ. This difficulty is overcome by assuming that within some small distance x_0 some other law applies, while beyond it the relation given above holds good. Langmuir[15] has shown that whether the force betweeen the surface and x_0 be assumed to be constant or to increase parabolically from zero, the result is the same and the work to reach x_0 is $W = e^2/4x_0$ and then

$$\phi = \frac{e^2}{4x_0} + \frac{e^2}{4x_0} = \frac{e^2}{2x_0}.$$

A simple calculation will show that the work required to remove an electron to a distance $10\,x_0$ is 19/20 that needed to remove it to infinity. Thus the factors operating in this region close to the surface are the ones most effective in modifying the work function of the metal and the emission of electrons.

For a perfectly smooth, homogeneous surface, the electric field is constant at any distance outside it, and the work function is constant over it. If, instead of the surface being homogeneous, it consisted of single, isolated atoms of one metal distributed regularly over the surface of the foundation metal, the electric field at atomic distances would be disturbed by the effect of the contact potential between the two metals. However, at a distance of several atomic diameters the field would be very nearly uniform and consequently ϕ would be nearly constant for the whole surface.

The third possible distribution capable of any sort of study would consist of patches of the electropositive material distributed at random over the surface of the other. If such a patch consisted of many hundreds of atoms, it would appear to an electron at a distance $10\,x_0$ normally out from the center of the patch as an infinite plane, and the field acting on the electron, and consequently the work function as applied to that electron would be a perfectly definite magnitude, characteristic of the patch material. Between the patch and the basic metal there would be a potential difference equal to the

[15] Langmuir, Trans. Am. Electrochem. Soc. **29**, 125 (1916).

C.D.P. between the two metals. Let Fig. 4-I represent such a surface. The shaded portions are patches of thorium and the adjacent areas tungsten.

Between these two there is a potential difference of about two volts (assumed since ϕ_0 for full activation is 2.6 volts and for clean tungsten is 4.5 volts). There will be lines of force originating on the thorium, as shown on the diagram. The effect of the fields of force will be to aid electrons to escape from the tungsten but to hinder their escape from the the thorium. Since we assume the electrons under consideration to come exclusively from the thorium, the first effect can be ignored. The retarding action will be more pronounced near the edge of the thorium areas, falling off rapidly as we move toward the center of the patch, and becoming fairly constant and negligible over the central portion.

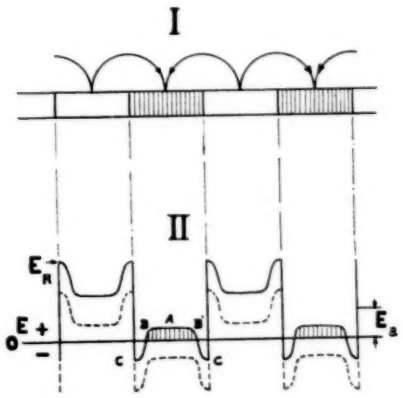

Fig. 4.

Let the dotted line of Curve II–Fig. 4 represent the field resulting from the C.P.D. between thorium and tungsten. The exact shape of the field distribution is indeterminate, but the one shown should be approximately correct. Assume for the present the electrons all to have zero initial velocities. If an external field E_a be applied, the combined effect of this and the "patch field" will be that of the solid line (Fig. 4–II). The shaded area represents the portion of the field accelerating electrons away from the surface. The length defined by it along the abscissa axis represents the part of the thorium covered surface from which electrons can escape from the surface under the influence of the applied field E_a. As E_a is increased from zero, emission begins as soon as the heavy solid line appears above the E_0 axis. Since the center portion of this curve is shown as flat, the area from which electrons can escape increases first rapidly with the voltage, then more and more slowly until finally the whole of the resultant field is in the direction to accelerate electrons away from the metal. At this point, the whole area of the thorium patch is an effective emitter, and the applied field is just strong enough to overcome the maximum field between thorium and tungsten at the point of contact of the two areas. This critical field is independent of the fraction of the surface covered with thorium so long as there remain exposed lines of contact of the two metals.

It should be characteristic only of the C.D.P. between the two metals concerned, and should vary for different pairs of elements.

If now the electrons be assumed to have a Maxwellian distribution of velocities, characteristic of the temperature, investigation with retarding fields should show a perfectly normal distribution curve for the portion BAB' and since we have assumed this line nearly flat, falling off sharply at B and B', the distorting effect of the patch field should be a minimum. As zero is approached and the shoulder of the curve BC begins to emit, the Maxwellian curve will be distorted by the increasing effective area of the thorium brought into action.

Application of this analysis to the typical curve of Fig. 3 shows agreement of the postulated theory and the experimental result throughout the length of the curve. Retarding fields show a Maxwellian distribution. In the neighborhood of zero potential a saturation current is reached, modified by the neutralization of the patch field by the applied field and by the Schottky effect. The patch effect is less and less important with increasing fields until at the point. V_1 (Fig. 1) the whole patch area emits and above this there is saturation emission, increased by the Schottky correction. It will be evident that for some distance above V_1 Schottky's relation will apply only approximately, as the field effective in reducing the surface work function is the difference between the field applied and the field due to the proximity of the tungsten, which is non-uniform over the area of the thorium patch. At very high applied voltages, where the patch field becomes negligible, Schottky's equation should represent the results with very satisfactory accuracy.

The choice of the point V_c as the zero of potential in the contact potential curve (Fig. 3) may need some justification. The point D, lying as it does on the actual curve, would seem at least an equally appropriate reference point, since only *changes* in contact potential are involved. However, the accuracy with which it can be determined is much less. Moreover, this point is modified by the velocity distribution of electrons and is therefore dependent on the temperature. Its sharpness of definition depends upon the shape of the shoulder of the curve E_R (Fig. 4-II). The extrapolated intersection at V_c is much less open to these objections. Also, due to the steepness of the slope of the portion $C\ D$ (Fig. 3) and the flatness of $A\ V$, the uncertainty in the line $A\ V$ due to its actual curvature introduces only a slight error in the determination of the hypothetical zero of potential at V_c.

It is important to note that the necessity of assuming a patch field even for a fully activated surface leads to the conclusion that the tungsten is never fully covered, but that there exist a maximum number of thorium areas distributed over the surface. If the break at V_1 (Fig. 1) is a constant for thorium on tungsten and this field is equal to the maximum retarding field exerted on electrons at the edge of the thorium areas by the tungsten atoms, this field should be of the order of magnitude of the C.D.P. (circa 2 volts) divided by some length which is of the same magnitude as that of the patches. For any different combination of elements, this critical field V_1 should have a different constant value. Thus for caesium on tungsten it should be larger, presumably in proportion to the larger contact difference in potential.

On the basis of this theory there seems to be a real significance to Dushman's extrapolation of the Schottky line to zero field to obtain i_0. This represents the emission from the actual area of electropositive metal present, free from the effects of both the "patch field" and the applied field, and is characteristic of the work function of the surface under consideration.

I take pleasure in acknowledging my indebtedness to the Charles A. Coffin Foundation, since most of the present investigation was carried out while holding one of its Fellowships at Princeton University. Also I tender sincere thanks to Professor K. T. Compton, under whose direction this research was conducted, and whose contributions were many and invaluable; to Dr. S. Dushman, of the General Electric Research Laboratories, for suggestions and criticism; to others in the Laboratories of that company for assistance in preparing apparatus; and to Mr. Robert W. Graves for aid and collaboration during part of the work.

Note added with proof: Since sending this paper to the publisher, these results have been discussed with Dr. Langmuir who has extended his calculations on the properties of a patch surface and reaches conclusions which are in complete disagreement with the observed facts on the Schottky effect. The explanation of this inconsistency between the theoretical deductions and the observations is to be included in a joint report in preparation by Dr. Langmuir and Professor Compton to be published in a forthcoming number of the Physical Review Supplement.

THE TEMPERATURE DEPENDENCE OF FIELD CURRENTS

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Abstract

The increase in the field current observed by Millikan and Eyring to take place at about 1000°K is shown to be of the order of magnitude of the thermionic emission to be expected from a thoriated filament at this temperature. The author considers that the results of Millikan and Lauritsen are inconclusive and do not definitely establish the existence of a dependence of field currents upon temperature. The author has carried out new experiments using an improved method of investigation and has been unable to detect any temperature variation in the field current. His contention is not that no temperature variation exists but that no real variation has yet been observed.

ALL investigators[1] are agreed that from 80°K to 1000°K the autoelectronic, or field, emission is independent of temperature. There is however a difference of opinion about the existence of a temperature dependence above 1000°K. Millikan and Eyring[2] observed an increase in the emission at this temperature but, by separating out the thermionic from the field current in a mixed emission, I found[3] that the field current showed no systematic increase with temperature and therefore concluded that the increase observed by Millikan and Eyring was due to the occurrence of a thermionic emission. Millikan and Lauritsen[4] have recently stated that the increase in emission observed by Millikan and Eyring "is about a billion times too large to be so interpreted;" this statement is evidently based on the emission characteristics of pure tungsten and disregards the fact that Millikan and Eyring used thoriated filaments. The thermionic emission from a thoriated tungsten filament is in fact of the order of magnitude of the increase observed by Millikan and Eyring, as may be seen from the following considerations.

The Results of Millikan and Eyring

The diameter of the filament used by Millikan and Eyring was 0.00123 cm. Its length is not stated but from the relative dimensions in their diagram it appears to have been of the order of 5 cm, giving a surface area of 0.019 cm.[5]

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[1] J. E. Lilienfeld, Ber. d. Sächs. d. Wiss. **72**, 31 (1920). B. S. Gossling, Phil. Mag. **1**, 609 (1926). R. A. Millikan and C. F. Eyring, Phys. Rev. **27**, 51 (1926).

[2] R. A. Millikan and C. F. Eyring, Phys. Rev. **27**, 51 (1926).

[3] N. A. de Bruyne, Proc. Cambs. Phil. Soc. **24**, 347 (1928).

[4] R. A. Millikan and C. C. Lauritsen, Phys. Rev. **33**, 598 (1929).

[5] S. Dushman, Gen. Elect. Rev. **26**, 156 (1923).

Thermionic emission from a fully thoriated wire at 1100°K is[5] 2.51×10^{-6} amps per cm^2 corresponding to an emission of 4.77×10^{-8} amps from an area of 0.019 cm.^{2} The Schottky effect at a field of 0.7×10^{6} volts per cm would increase the thermionic emission to 1.35×10^{-6} amps; at this field Millikan and Eyring observed an increase in the emission of 0.02×10^{-6} amps. At a field of 1.0×10^{6} volts/cm the thermionic emission would be 2.58×10^{-6} amps while the observed increase was 3.0×10^{-6} amps. The thermionic emissions have been computed for a fully thoriated surface, but taking into account the uncertainties in the measurements the observed increases appear to be of the order of magnitude of the possible thermionic currents, even if the surface were not completely thoriated. The experiments of Millikan and Lauritsen do not therefore establish the existence of a dependence of the autoelectronic emission on temperature.

The Results of Millikan and Lauritsen

Millikan and Lauritsen[4] have recently published some new data in which proper allowance can be made for the thermionic emission taking into account the Schottky effect. Unfortunately the new data are limited to one graph in which only two points are relevant. Up to 800°K the current was constant at 4.6×10^{-8} amperes, at 1130°K (a temperature at which the thermionic current was negligible) the current was 5.6×10^{-8} amperes, at higher temperatures a thermionic current set in. These results therefore show a temperature variation which cannot be explained as due to a thermionic emission. Yet the position as left by the publication of Millikan and Lauritsen's paper is far from satisfactory, since it is impossible to have any confidence in a conclusion based on a few measurements of an effect in which it is extremely difficult to obtain reproducible results.

Author's First Results

I first repeated Millikan and Lauritsen's experiment. A constant voltage was applied to a tube and the filament temperature was raised and lowered rapidly in fixed steps, the emission being noted at each step. The voltages used varied between 12,000 and 23,000 volts. A number of experimental runs were carried out. The results were quite inconclusive; two showed an increase in the autoemission at 1100°K of the order of magnitude observed by Millikan and Lauritsen, one showed a decrease in the emission, but the majority gave a series of widely scattered points through which it was impossible to draw any smooth curve; in general the spontaneous fluctuations in the emission were found to be of the order of magnitude of the increase observed by Millikan and Lauritsen. In plotting characteristics showing the variation of emission with field these fluctuations are far less disturbing because of the tremendous increase in the current produced by a comparatively small rise of field, but in an experiment such as this where the field is kept constant the spontaneous variations become relatively important. It was obvious that a new method of attack was required, and it was decided to obtain a continuous record of the galvanometer deflection.

Results by Improved Method of Investigation

The author observed that in some tubes the filament changed its shape considerably when heated and that such distortion was accentuated when a strong field was applied. The same difficulty has been noted by I. Langmuir and K. H. Kingdon[6] in their work on contact potentials. The author therefore used tungsten wire of 0.02 mm diameter instead of the finest wire available. The filament of length was formed into a stable sharp angled loop inside a cylindrical anode closed at one end. The filament leads were encased in glass leaving only the filament exposed. The tubes were exhausted under the same conditions as a transmitting valve, the filament was outgassed and the anode was kept at bright red heat for twenty minutes before sealing off. After sealing off the filament was lit for some time with an applied anode voltage of 10,000 volts.

The galvanometer deflection was recorded photographically on a rotating drum which revolved once in about two minutes. A constant voltage from a valve rectifier set was applied to the experimental tube and the filament temperature was raised, for periods of about ten seconds, from room temperature to some other higher temperature which was fixed for each run. The periods when the filament was hot were recorded on the drum by the lighting of a small lamp which left a trace on the photographic paper. A calibration and zero line were also recorded. In all the curves the time axis increases from right to left.

Fig. 1. Galvanometer record. Applied potential 5,500 volts, filament heating current 0 and 0.235 amp.

Fig. 1 shows the record obtained when the voltage was too low to produce an autoemission. The small regular rises in the emission correspond to the periods when the filament temperature was raised to 0.235 amps [giving a temperature of 1600°K approximately]; 5500 volts were applied to the anode. It will be seen that at 5500 volts a measurable thermionic emission begins at a filament current of 0.235 amps.

Figs. 2, 3, 4, 5 show results obtained with an applied potential of 17,800 volts (corresponding to a field strength of 1.4×10^6 volts per cm). The first signs of any correlation between the emission and the periods of heating occur between a filament current of 0.220 and 0.230 amps. i. e. between 1550°K and 1600°K; it is in just this temperature range that a thermionic current is to be expected.

Figs. 6, 7, 8, 9, 10 show results obtained at an applied potential of 14,800 volts corresponding to a field of 1.2×10^6 volts per cm. Here again the first signs of any increase occur when the filament current is raised to 0.230 amps, corresponding to a filament temperature of 1590°K. Thus no measurable

[6] I. Langmuir and K. H. Kingdon, Phys. Rev. **34**, 129 (1929).

increase in the autoemission takes place up to about 1600°K at which temperature a thermionic emission sets in.

It seems probable that the electrons pulled out by strong fields must come in the main from energy levels lower down than those from which the ther-

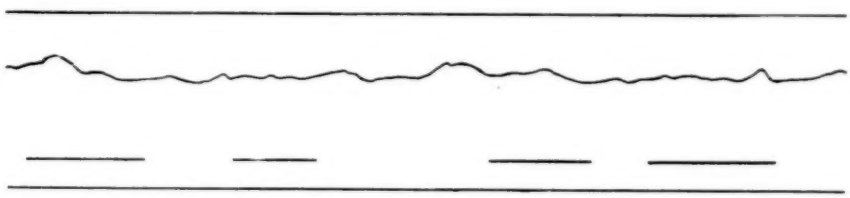

Fig. 2. Filament heating current 0 and 0.190 amp.

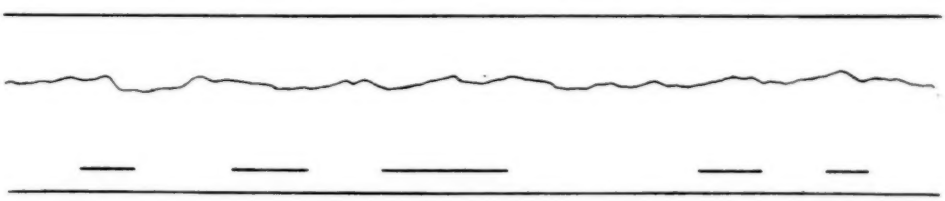

Fig. 3. Filament heating current 0 and 0.200 amp.

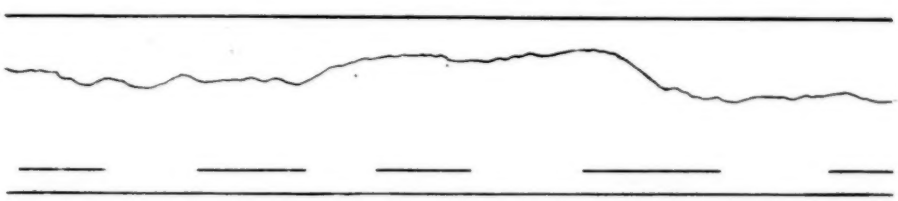

Fig. 4. Filament heating current 0 and 0.220 amp.

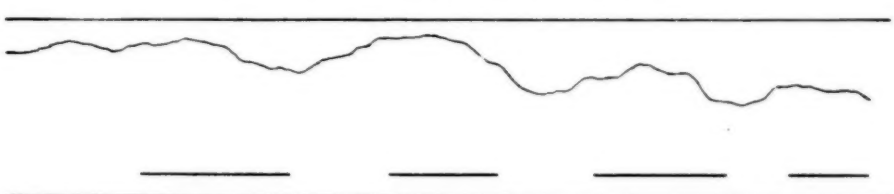

Fig. 5. Filament heating current 0 and 0.231 amp.

Figs. 2, 3, 4, 5. Galvanometer records with 17,800 volts applied to filament. The top horizontal line represents a current of 2 microamperes, the irregular line gives the electronic emission, the broken lines the periods of heating the filament, and the bottom line the galvanometer zero.

mionic emission takes place, since within the limits of experimental error the autoemission is independent of temperature. Unfortunately Sommerfeld's theory can give no information on the temperature dependence, beyond showing that it must be small, since no exact measurement of the applied field is yet possible.

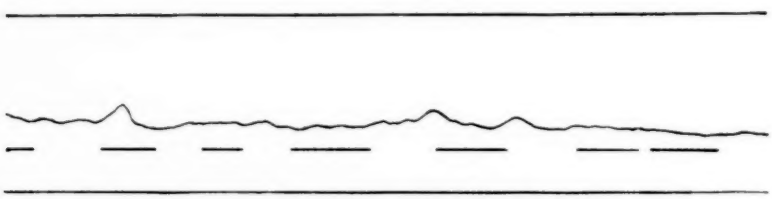

Fig. 6. Filament heating current 0 and 0.195 amp.

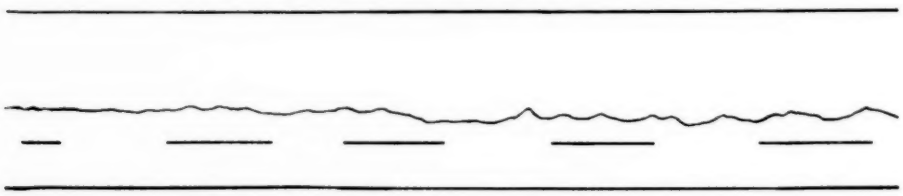

Fig. 7. Filament heating current 0 and 0.202 amp.

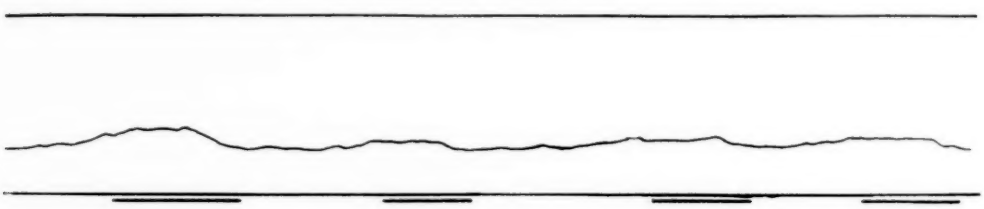

Fig. 8. Filament heating current 0 and 0.230 amp.

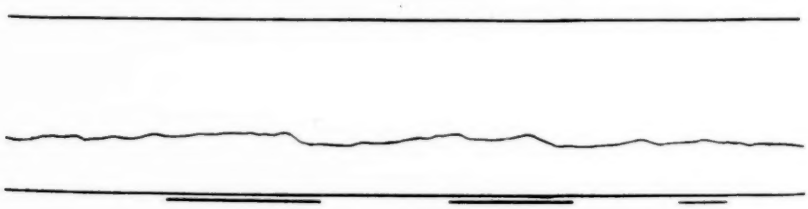

Fig. 9. Filament heating current 0 and 0.235 amp.

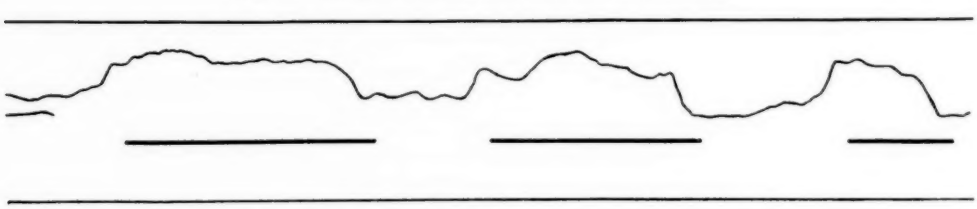

Fig. 10. Filament heating current 0 and 0.248 amp.

Figs. 6, 7, 8, 9, 10. Galvanometer records with 14,800 volts applied to the filament. The top horizontal line represents a current of 2 microamperes, the irregular line represents the electronic emission, the brken lines the periods of heating of the filament, and the bottom line the galvanometer zero.

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VARIABLE FLOW IN PIPES

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Abstract

The problem considered is that of finding a variable pressure gradient or forced motion of the pipe in a longitudinal direction which, at the time when it ceases to act, will have produced a prescribed distribution of velocity over the cross-section of the pipe. The subsequent changes in the distribution as the motion decays are also investigated and the cases examined point to the conclusion that an initial velocity profile with curvature of one sign will retain this property as it changes into the profiles for the different stages of the decaying motion.

Introduction

THE subject of variable flow in pipes is of much importance in engineering and has been studied experimentally in the case when the motion is turbulent. The problems which arise in connection with the metering of gases have been ably discussed by Hodgson,[1] Swift,[2] Judd and Pheley.[3] Accelerated flow without pulsations has been studied by Gibson[4] and Aisenstein[5] who express the time necessary to reach a velocity v in the form

$$t=(K/2V)\log\frac{V+v}{V-v}$$

where V is the final velocity of steady flow under the force or pressure gradient which produces the constant acceleration and K is a coefficient which has one value for the Poiseuille régime and another value for the Venturi or turbulent régime, K depending in each case upon the value of the Reynolds number at time t.

We shall study here problems relating to flow in the Poiseuille régime when the acceleration is variable. For simplicity the compressibility of the fluid is neglected. This is undoubtedly a defect because in the particularly interesting case of rapid oscillations the motion will be complicated by the propagation of waves.

The propagation of waves in water has been much studied in connection with the phenomenon of water hammer in pipes and need not be discussed here. The propagation of air waves along a pipe, when viscosity is taken into consideration, has been studied theoretically by Stokes, Kirchhoff and Rayleigh.[6]

[1] Hodgson, Proc. Inst. Civil Engineers **204,** 108 (1916–17).
[2] Swift, Phil. Mag. (7) **5,** 1 (1928).
[3] Judd and Pheley, Mech. Eng., **45,** 223, 270 (1923).
[4] Gibson, "Water hammer in hydraulic pipe lines," p. 50.
[5] Aisenstein, Trans. Amer. Soc. Mech. Eng. **51,** 67 (1929).
[6] See Lamb's Hydrodynamics, pp. 612–617.

The recent experiments of Simmons and Johansen[7] indicate, however, that there is need of further mathematical investigations. The author is considering the problem of pulsations when both viscosity and compressibility are taken into consideration but the work is not sufficiently advanced to warrant publication.

1. *Free decay, motion initially prescribed.* A long straight pipe of uniform cross-section has its ends attached by flexible connections to two reservoirs containing water, the pipe itself being supposed to be at any time completely filled with water.

The pipe is now moved in the direction of its length with a varying velocity $P(t)$. If u is the velocity of the water at the point (x,y,z) at time t the direction of motion being that of the axis of x, the equation of motion of the water relative to axes fixed relative to the reservoirs is

$$\rho\frac{\partial u}{\partial t}=\mu\left(\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\right)-\frac{\partial p}{\partial x}+\rho X$$

where p is the pressure, ρ is the density of the water, μ its viscosity and X the external force per unit mass. If the water is treated as incompressible and the pipe as rigid, the equation of continuity

$$\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x}(\rho u)=0$$

reduces to $\partial u/\partial x=0$ and implies that $u=F(y,z,t)$. We shall assume moreover that ρ and μ are constants independent of position and of the time t.

If we write $u=U+P(t)$ where U is the velocity of the water relative to the pipe, the equation for U is

$$\rho\frac{\partial U}{\partial t}=\mu\left(\frac{\partial^2 U}{\partial y^2}+\frac{\partial^2 U}{\partial z^2}\right)-\frac{\partial p}{\partial x}-\rho\frac{dP}{dt}+\rho X$$

and so the motion relative to the pipe is the same as if the pipe were at rest and the fluid acted upon by an additional body force $-P'(t)$ per unit mass or an equivalent pressure gradient $\rho(P't)$. When p and X are zero the free motion in an oscillating pipe is relatively the same as the forced motion in a stationary pipe when the external force or pressure gradient fluctuates in the prescribed manner.

The transfer of motion from an oscillating plane to an adjoining liquid has been studied by Stokes,[8] Rayleigh[9] and other writers. Stokes showed that when the frequency of oscillation is high the motion in the fluid rapidly diminishes in intensity as the distance from the plane increases. This indicates that if fluid bounded by parallel plane walls is set in motion by a rapidly fluctuating pressure gradient which oscillates about a zero value, the

[7] Simmons and Johansen, British Advisory Committee for Aeronautics, R & M. 957 (1925).

[8] Stokes, Cambr. Phil. Trans. **9** (1850).

[9] Rayleigh, Phil. Mag. (6) **21**, 697 (1911).

distribution of velocity over the cross-section will be approximately uniform except in the immediate neighbourhood of the walls, where rapid variations are to be expected. This result has been extended by S. F. Grace[10] to the case of flow in a pipe of circular section. For a pipe of radius 1 cm there is approximate uniformity in the distribution of velocity over a large part of the cross-section if the period of oscillation is less than six seconds. The velocity moreover, lags 90° in phase behind the force producing the motion.

The existence of a phase lag indicates that the water may still be moving when the driving force has ceased to act. If, then, we go back to the case of the moving pipe we can say that the water may still be moving when the pipe is brought to rest. The velocity distribution at this time ($t=0$, say) may, indeed, be prescribed more or less arbitrarily so long as the velocity at the boundary is zero. Some interesting questions now arise with regard to the manner in which the velocity profile changes as the motion dies down.

Suppose, for instance, that the velocity profile has initially curvature of only one sign so that, when the velocity at each point of the cross-section is represented by an ordinate MQ, the locus of Q is everywhere concave to the plane of the section. It is interesting to inquire whether at some later time t the velocity profile can be partly convex to the plane of the section This question is an interesting one because in his studies of the stability of. an inviscid incompressible fluid in rectilinear motion between parallel planes Lord Rayleigh[11] found that a steady motion, without changes in the sign of the curvature of the velocity profile, was stable for small oscillations but that a profile with changes in the sign of the curvature might be unstable.

The question has been studied for the case of flow between parallel planes $z=\pm a$, the free motion being represented by

$$u=c_1e^{-s}\cos\theta+c_3e^{-9s}\cos 3\theta+c_5e^{-25s}\cos 5\theta+\cdots$$

where $s=\nu\pi^2t/4a^2$ and $\theta=\pi z/2a$. The expansion was limited to the first three terms and the coefficients c_1, c_3, c_5 were chosen so that the coefficients of z^2 and z^4 in the Taylor series for u were initially zero. This gives an initial distribution of velocity with curvature of one sign and a nearly constant value for a large part of the cross-section. The numerical work gave no indication of a change in sign of the curvature at any point of the profile as it changed with the time. The profile, in fact, gradually approached the shape of the cosine curve $u=k\cos\theta$ which differs only slightly in shape from the parabola characteristic of steady motion.

The question was also examined by assuming that at time $t=0$

$$d^2u/dz^2=-\cos\theta\ [(\alpha\cos^2\theta+\beta)^2+\gamma^2]$$

where α, β and γ are constants. Again there was no indication that at a later time t it would be legitimate to write

[10] Grace, Phil. Mag. (7) **5**, 933 (1928).

[11] Rayleigh, Proc. London Math. Soc. **10**, 4 (1879); **11**, 57 (1880); **19**, 67 (1887); **27**, 5 (1895); Phil. Mag. **34**, 59 (1892); **26**, 1001 (1913); **28**, 609 (1914). See also, L. Prandtl, Ziets. f. Angew. Math. und Mech. **1**, 431 (1921).

$$d^2u/dz^2 = -\sigma \cos\theta \ [\cos^2\theta - \cos^2\theta_1][\cos^2\theta - \cos^2\theta_2]$$

where θ_1 and θ_2 are real angles.

In the work of Grace the oscillations were undamped. To discuss a type of variable motion which ceases at time $t=0$ we first consider the case in which

$$P(t) = (-\nu t)^{-1/2} \exp(m^2/4\nu t) \quad t<0,$$
$$P(t) = 0 \qquad\qquad\qquad\qquad t>0,$$

where $\nu = \mu/\rho$ is the kinematic viscosity. Since $\partial u/\partial t = \nu \partial^2 u/\partial z^2$ and

$$P(t) = K\int_0^\infty e^{\xi^2 \nu t} \cos(m\xi) d\xi, \quad t<0,$$

where $K = 2/\sqrt{\pi}$, an appropriate solution is

$$u = K\int_0^\infty e^{\xi^2 \nu t} \cos(m\xi) \cosh(z\xi) \operatorname{sech}(a\xi)\, d\xi \quad t<0.$$

As $t\to 0$, $u\to u_0$, where

$$u_0 = K\int_0^\infty \cos(m\xi) \cosh(z\xi) \operatorname{sech}(a\xi) d\xi$$
$$= \frac{(2K/a) \cosh(m\pi/2a) \cos(z\pi/2a)}{\cosh(m\pi/a) + \cos(z\pi/a)}.$$

When $\sinh^2(m\pi/2a) = \frac{1}{2}$ u_0 is approximately constant over a considerable part of the cross-section. If, however, we take $\pi^2 m^2/4a^2 = 1/32$, we have the result that u_0 is approximately proportional to

$$\frac{65\cos\theta}{4+128\cos^2\theta}.$$

When $z=0$ this fraction is equal to $65/132$ and when $z=2a/3$ the fraction is equal to $65/72$. It should be noticed that the maximum value of $P(t)$ occurs when $2\nu t = -m^2$, the maximum value being $(m^2 e/2)^{-1/2}$. Hence a small value of m corresponds to a large maximum velocity of the walls.

The present result confirms our statement that the fluid may still be moving when the pipe has ceased to move.

To discuss the decay of the motion when $t>0$ we expand u_0 in the form

$$u_0 = H\sum_{s=0}^\infty (-)^s e^{-mS} \cos(zS)$$

where $S = \pi(2s+1)/2a$ and $H = 4\sqrt{\pi}/a$. The velocity at time t is then

$$u = H\sum_{s=0}^\infty (-)^s e^{-mS - \nu S^2 t} \cos(zS).$$

Since u satisfies the equation $\partial u/\partial t = \nu \partial^2 u/\partial z^2$ the velocity $u^{(n)}$ corresponding to a function

$$P^{(n)}(t) = \frac{\partial^n}{\partial t^n} P(t)$$

$$u^{(n)} = \nu^n \frac{\partial^{2n} u}{\partial z^{2n}}$$

is

$$= K\nu^n \int_0^\infty e^{\xi^2 \nu t} \xi^{2n} \cos(m\xi) \cosh(z\xi) \operatorname{sech}(a\xi) d\xi \quad (t<0)$$

$$= H\nu^n \sum_{s=0}^{\infty} (-)^{s+n} S^{2n} e^{-mS - \nu S^2 t} \cos(zS) \quad (t>0).$$

An initial distribution of velocity

$$\overline{u}_0 = H \sum_{s=0}^{\infty} (-)^s \phi(-\nu S^2) e^{-mS} \cos(zS)$$

will, with a suitable form of the function ϕ, be produced by a velocity of the walls varying up to time 0 according to the law

$$\overline{P}(t) = \phi\left(\frac{\partial}{\partial t}\right) P(t).$$

2. *Forced motion.* We next consider the equation

$$\rho \frac{\partial u}{\partial t} = \mu \frac{\partial^2 u}{\partial z^2} - \frac{\partial p}{\partial x}, \quad (\mu = \rho\nu)$$

for the rectilinear flow of an incompressible viscous fluid of constant density ρ when the pressure gradient $\partial p/\partial x$ varies with the time. For convenience we write

$$-\frac{\partial p}{\partial x} = \left(\frac{2\mu}{\pi}\right) \int_0^\infty e^{-\nu m^2 t} \cos ma \cdot dm \int_0^\infty \cos mv \, \phi(v) dv$$

where $\phi(v)$ is an even function for which Fourier's integral formula may be used with confidence. The corresponding expression for u is then

$$u = (2/\pi) \int_0^\infty e^{-\nu m^2 t} (\cos mz - \cos ma)(dm/m^2) \int_0^\infty \cos mv \, \phi(v) dv.$$

It should be noticed that at time $t=0$ we have

$$-\frac{\partial p_0}{\partial x} = \mu\phi(a)$$

$$u_0 = \int_z^a ds \int_0^s \phi(v) dv.$$

If, on the other hand we write $f(m)$ instead of $\int_0^\infty \cos mv\,\phi(v)dv$ and take $f(m)=1$ we have

$$-\frac{\partial p}{\partial x}=\mu(\pi\nu t)^{-1/2}e^{-a^2/4\nu t}, \qquad \text{and}$$

$$u=(\pi\nu t)^{-1/2}[F(a,t)-F(z,t)], \qquad \text{where}$$

$$F(z,t)=\int_0^z (z-s)e^{-(s^2/4\nu t)}ds.$$

A short table of values of $F(z, t)/2\nu t$ is given below. For convenience n has been written for $z/2(\nu t)^{1/2}$ and values of e^{-n^2} are also included. The fifth figure in the decimal may be slightly incorrect.

TABLE I

n	$F(z, t)/2\nu t$	$\exp(-n^2)$
0	0	1
0.1	0.00999	0.99005
0.2	0.05974	0.96079
0.3	0.08866	0.91393
0.4	0.15587	0.85214
0.5	0.24009	0.77880
0.6	0.33992	0.69768
0.7	0.45361	0.61263
0.8	0.57959	0.52729
0.9	0.71611	0.44486
1.0	0.86156	0.36788
1.1	1.01436	0.29820
1.2	1.17313	0.23693
1.3	1.33668	0.18452
1.4	1.50399	0.14086
1.5	1.67401	0.10540
1.6	1.84608	0.07731
1.7	2.02000	0.05557
1.8	2.19489	0.03916
1.9	2.37055	0.02705
2.0	2.54666	0.01832

For the case in which $a=2$ the distribution of velocity has been calculated at times t for which $2(\nu t)^{1/2}$ has the values 1, 2, 4, respectively and compared with the parabolic distribution for steady flow. In each case the velocity is compared with the axial value c. The third time is beyond that at which the pressure gradient is a maximum. It will be noticed that while the pressure gradient is increasing the distribution of velocity differs only slightly from the distribution for steady flow. When t is large we have $F(z, t)=z^2/2-z^4/48\nu t$, approximately, and so in the final stages of the motion the distribution of velocity again differs only slightly from the parabolic distribution.

TABLE II

	z/a						
$2(\nu t)^{1/2}$	0	0.2	0.4	0.6	0.8	1	
1	1	0.9384	0.7724	0.5393	0.2751	0	u/c
2	1	0.9307	0.8191	0.6054	0.3273	0	u/c
4	1	0.9584	0.7512	0.6307	0.3508	0	u/c
Parabola	1	0.96	0.79	0.64	0.36	0	u/c

3. The analysis for rectilinear flow in a tube of circular section is very similar to that for flow between two parallel walls. The equation of motion is now

$$\rho \frac{\partial u}{\partial t} = \mu \left(\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} \right) - \frac{\partial p}{\partial x},$$

where r is the distance of a point from the axis of the tube. We shall commence with a study of forced motion.

If

$$-\frac{\partial p}{\partial x} = \mu \int_0^\infty e^{-\nu m^2 t} J_0(ma) m dm \int_0^\infty J_0(mv) \psi(v) v dv$$

where $\psi(v)$ is a function for which the inversion formula of Hankel may be used with confidence, the corresponding expression for u is

$$u = \int_0^\infty e^{-\nu m^2 t} [J_0(mr) - J_0(ma)] (dm/m) \int_0^\infty J_0(mv) \psi(v) v dv$$

and at time $t = 0$ we have

$$-\frac{\partial p}{\partial x} = \mu \psi(a)$$

$$u_0 = \int_r^a (ds/s) \int_0^s v \psi(v) dv.$$

Another particular case of interest is that in which

$$-\partial p/\partial x = (\mu/2\nu t) \exp [-a^2/4\nu t] = \mu \int_0^\infty e^{-\nu m^2 t} J_0(ma) m dm$$

$$u = \int_t^\infty (d\tau/2\tau) [\exp (-r^2/4\nu t) - \exp (-a^2/4\nu t)].$$

Next, taking the case of free motion, let us suppose that the velocity of the pipe at time t is given by the function $P(t)$, where

$$P(t) = (-1/2\nu t) \exp (g^2/4\nu t) \quad t < 0$$

$$P(t) = 0 \quad t > 0$$

Since

$$P(t) = \int_0^\infty e^{\nu m^2 t} J_0(mg) m dm \quad t < 0$$

an appropriate solution is

$$u = \int_0^\infty e^{\nu m^2 t} J_0(mg) m dm [I_0(mr)/I_0(ma)], \quad t < 0$$

with the usual notation for the Bessel function with imaginary argument. As $t \to 0$, $u \to u_0$, where

$$u_0 = \int_0^\infty J_0(mg) m dm [I_0(mr)/I_0(ma)]$$

IONIC MOBILITIES IN Cl_2 AND IN Cl_2–AIR MIXTURES

By Leonard B. Loeb
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(Received December 9, 1929)

Abstract

Work of early investigators and of Herbert Mayer indicates that the presence of traces of Cl_2 reduces the mobility of the negative ion below that of the positive ion, a fact which appeared inconsistent with a theory of Condon and the writer. No investigations of mobilities of both ions in pure Cl_2 have been reported. The possibility that the discrepancy between theory and observation in Mayer's results was caused by HCl in the Cl_2 made a more careful investigation imperative. Cl_2 carefully prepared and free from both HCl and H_2O was used. It was found that the values of the mobilities in pure Cl_2 on the new absolute standard for positive and negative ions was 0.654 and 0.510 cm/sec per volt/cm respectively. A study of mixtures of dry air and Cl_2 showed that traces of Cl_2 less than 0.1 percent reduce the negative mobility below that of the positive ion. The positive mobilities were little affected by the presence of Cl_2 so that while positive ions obey Blanc's law in Cl_2-air mixtures the negative ion shows a marked clustering effect. No disturbances due to dipole moments were observed for positive ions in Cl_2 as is to be expected.

Introduction

IN ATTEMPTING to determine something of the nature of the gaseous ions a study of mobilities of ions in gaseous mixtures has shown itself to be of value.[1] Later investigations have shown that beyond the more important conclusions already drawn from this study, further investigations will add but little of importance, until a much greater control of minute traces of impurity can be had.[1,2] This appears to be the more so in view of the recent researches of Erikson.[3] Before concluding the work on mixtures and turning to a new method of attack on the ion problem it was felt essential to study one more gas, to wit: chlorine, in view of certain apparent discrepancies in data and theory. So far ionic mobilities in pure chlorine have been studied by only one observer, Wahlin,[4] and that for the *negative ion* only. His value for the negative ion mobility constant was 0.73 cm/sec per volt/cm. The interest in Cl_2 lies in the fact that all observers have reported[5] that the *negative* mobility in Cl_2 appeared to be *less than* the *positive* mobility while according to Condon

[1] L. B. Loeb, Phys. Rev. **32,** 81 (1928).
[2] DuSault and Loeb, Proc. Nat. Acad. Sci. **14,** 384 (1928).
[3] H. A. Erikson, Phys. Rev. **34,** 635 (1929).
[4] H. B. Whalin, Phys. Rev. **19,** 173 (1922).
[5] To date no accurate observations on *both* ions in Cl_2 have been made. The effect of Cl_2 in mixtures of low percentage Cl_2 with other gases inferred by early observers and one very uncertain result of Mayer's at 8 cm pressure were the only data on which such assertions could be founded.

and the writer[6] this should not occur for gases having a low dipole moment fairly symmetrically placed inside of the molecule, as in Cl_2.

Early Attempts of the Writer

In closing the work on the mobilities in mixtures for the spring of 1928 Miss L. DuSault and the writer therefore made a study of Cl_2. In this case ordinary *grease lubricated stopcocks* were employed, and the Cl_2 was fractionated from a large tank loaned by the Chemistry department, liquid air being used, together with cooling traps to remove moisture. Two interesting facts were found in this work which was carried on with Cl_2 and occasionally Cl_2 mixed with H_2, using pure H_2 as a control gas for calibrating the apparatus. The one fact was that Cl_2 yielded a positive mobility constant of 0.617 cm/sec per volt/cm and a negative mobility constant of 0.466 cm/sec per volt/cm under the conditions used. This is one of the cases where the negative mobility relative to the positive mobility is as low as it has ever been observed and appeared contrary to the theory of Condon and Loeb. Further certain uncontrollable irregularities were observed in some of these cases in which the presence of traces of Cl_2 in pure H_2 caused phenomenally high values of the positive ion mobilities. An analogous result had been observed to a smaller extent in the SO_2–H_2[2] mixtures, but in the case of Cl_2 the values of the positive mobility were so high, (i.e. in one or two cases three times the normal mobility in H_2) that a further study seemed suitable.

In all these studies it was observed that when the ionization chamber was opened for cleaning to remove the last traces of Cl_2 a strong odor of HCl was present, even after prolonged pumping. This was found to be due to the extensive reaction of Cl_2 with the organic stopcock grease which emitted HCl for hours after exposure to Cl_2.

On resuming work in the fall of 1928, the abnormally high positive mobilities persisted in an unpredictable fashion, even after all the apparatus up to the mercury vapor pump had been carefully cleaned. At this stage of the work it had never been found essential to place a liquid air trap between the pump and the chamber as Hg vapor has no material effect on the ions. It then was suspected that the Cl_2 acting on the Hg had produced $HgCl_2$ which on heating in the pump gave off Cl_2 and so produced the spurious high values mentioned. On cleaning the pump and using fresh Hg no more values of this sort were observed. The facts which seemed apparent as far as the high values of positive mobilities were concerned could be summed up as follows. The presence of either traces of SO_2 or more especially Cl_2 from the mercury vapor pump in traces sometimes seemed to cause this effect which could never be controlled. It became an urgent problem to attempt to discover the cause of this effect if possible.

The low values of the negative mobilities in Cl_2 relative to the positive values, and the practically non-polar nature of Cl_2, led the writer to look for this lowering in the presence of HCl due to stopcock greases and due to HCl in the Cl_2 from the tank which could not be removed by fractionation.

[6] L. B. Loeb, Phys. Rev. **32**, 95 (1928). Also Kinetic Theory of Gases, p. 478.

The Preparation of Pure Cl_2

Beginning in the spring of 1929 and extending well into the autumn attempts were made to develop a system for generating Cl_2 free from H_2O and HCl, and devise greaseless stopcocks. The trouble with the use of mercury seal stopcocks lay in the large number of cocks required, the dangerous nature of large quantities of Cl_2 gas in case of failure of the mercury seal stopcocks and the constant "freezing" of such stopcocks with large pressure differences and constant use. The problem was finally solved as follows.

For the apparatus a large number of mercury seal type of stopcocks of a high quality were made for this work by Mr. L. B. Clark, then departmental glass blower. The design of these is shown in Figure 1. In place of ordinary

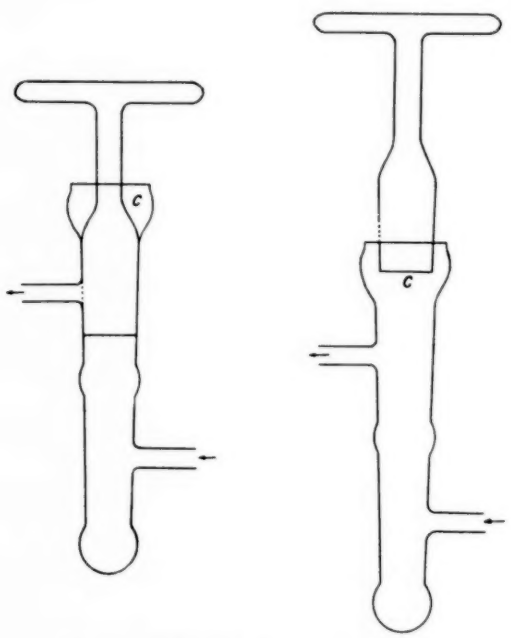

Fig. 1. Design of mercury-seal stopcocks.

lubricants a paste of P_2O_5 and water was made by dissolving as much P_2O_5 in a small amount of water as possible. This was achieved by heating to 250 or 300°C in a porcelain dish. The paste on cooling was like a very thick syrup in consistency. Trouble was experienced at first in that the P_2O_5 of *best quality* for drying tubes furnished by standard chemical concerns *contained marked amounts of* P_2O_3. On mixing with water local heating and steam production resulted in the reduction of P_2O_3 to P, which on heating or otherwise changed to the red form. The presence of this substance was confirmed by the dull red color, the odor and the flashes of flame at the surface of the paste as the temperature rose above 250°C. It might be noted that the pink color taken on by P_2O_5 in drying trains as it hydrates where organic matter is avoided is due to

the formation of this substance. By either getting a good grade of P_2O_5, which rarely happens, or by subliming the P_2O_5 for long hours at a reasonably low temperature, (below the melting point so as not to attack the glass) in a stream of O_2 the pentoxide may be prepared free from such substances. In the results to be given earlier measurement were made with P_2O_5 lubricant containing red phosphorus. The fear that Cl_2 might react in traces with P led to the use of later lubricants treated as above and free from this source of trouble. As it turned out the results were apparently not influenced by this impurity.

In using P_2O_5 paste as a lubricant care must be taken to have the moisture of the air kept from the paste on the stopcocks. Accordingly the surface of the P_2O_5 was covered with a pure mineral oil in the cup part *C* of the stopcocks. The system was always first dried out carefully before lubricating and replacing the stopcocks. As long as the gases inside were dry the lubricant on the beautifully ground stopcocks made for us behaved very well even under pressure differences of 1 atmosphere and with frequent turning. Gradually however the lubricant "worked" out of the cocks on constant use, (25 to 50 turnings over a period of a week) and had to be renewed.

The Cl_2 was generated by a method previously used by Professor Rollefson of the Chemistry department. $CuCl_2$ deprived of most of its water by heating and stirring under a hood was placed in heavy Pyrex glass bulbs surrounded by heating coils. These were heated in vacuo gradually beginning at 200°C for some 10 to 20 hours increasing the temperature step by step to 250° in 3 hours, to 300° in 3 more hours, to 350° in 4 hours and held at close to 400° for some 4 hours. Under these conditions no more water or HCl was observed to come off and Cl_2 began to appear. The temperature was then raised rapidly to from 450° 500° and the first fraction of Cl_2 was run down the drain by using a Nelson oil pump which permits the exhaust being run into a drainpipe of the sink directly. The pump with liquid air trap protecting it was then cut off and the Cl_2 generated into a trap cooled with liquid air. After enough had distilled over, the heat was reduced and the first fraction of the Cl_2 run into the trap protecting the pump by opening the proper stopcock. The central fraction was then distilled into a storage trap adjoining the mobility apparatus and kept frozen with liquid air until needed. The last fraction and the material in the protecting trap to the pump were then rapidly exhausted through the pump to the drain by warming the traps with the hand. The oil in pumps used this way needs frequent changing to prevent rusting of the pump due to the HCl from the reaction of the oil with Cl_2. In this way the experiments were carried on with no exposure to Cl_2 on the part of the workers although dangerously large quantities of liquid Cl_2 were used. When in removing the last parts of Cl_2-air mixtures by the Cenco and diffusion pumps from the ionization chamber into the air of the room the noxious effects of the Cl_2 in the room were considerably ameliorated by the free use of NH_4OH about the escape vents. The NH_3 gas by protecting mucous membranes from the action of HCl saved all the Cl_2 workers from bad chlorine colds.

The Measurements

In other respects the measurements were carried out by the standard methods employed by the writer [1, 2, 7] in other mixtures, except for the use of a liquid air trap between the mercury vapor pump and ionization chamber. A brand new freshly gold plated chamber was used for this work with a spring contact device to insure good metallic contact between the upper plate and the outside. In the previous designs the contact had been made by the pressure of the threads in the tube supporting the upper plate against the threads of the supporting rod. The chamber was made gas tight as before by a pressure joint on a lead gasket. To prevent slow leaks the *outside* of the lead joint at the gasket was covered with an oily heavily chlorinated hydrocarbon called commercially chloracosan, which does not react with Cl_2 and is employed medicinally for use in chlorine applications, as it does not react to form HCl. This was kindly suggested to the writer by Dr. Felix Lengfeld, formerly of the University of California.

The measurements were nearly all made using an auxiliary field with 12 volts between gauze and lower plate over 1.2 cm. The plate distance used was about 1.0 cm, and in most cases the alternating potential at which the ions crossed was fixed so as to be 30-40 volts. Where the ions crossed at lower or higher alternating potentials correction was made for the interpenetration of

Table I. *New measurements; pure Cl_2, Autumn 1929.*

Mobility constant (reduced to 760 mm, 20°C)		
$K+$	$K-$	
0.600	0.448	Stopcock lubricant free from red P
0.582	0.422	
0.600	0.532	Stopcock lubricant contained red P
0.606	0.490	
0.598	0.473	average

Table II. *First measurements of tank Cl_2, Spring, 1928 (in collaboration with L. DuSault).*

Ion	Mobility Constants				Average
$K+$	0.612	0.594	0.632	0.631	0.617
$K-$	0.472	0.452	0.456	0.482	0.466

fields[2,8] by multiplying by a factor corresponding to the change in mobility for the same alternating potential produced by a corresponding change in the auxiliary field. The same sort of correction was applied to the few results using an auxiliary field of 6 volts. The corrected results for the mobility constant for pure chlorine are listed below with comments.

[7] L. B. Loeb, Proc. Nat. Acad. Sci. **13,** 510 (1927); **14,** 193 (1928); **14,** 384 (1928); **15,** 146 (1929).

[8] L. B. Loeb, Jour. Franklin Inst. **196,** 537, and 771 (1923). Ann. d. Physik **84,** 689 (1927).

The Mobilities of Ions in Cl_2.

It is seen from Tables I and II that the values of the mobilities were closely the same in the early measurements and in those with purer Cl_2. It is also seen that the presence of red P in the lubricant did not change the values within the limits of error. The values were all averaged together, the newer values being weighted twice the old ones. This gives the final values as 0.604 cm/sec per volt/cm for positive ions and 0.471 cm/sec per volt/cm for negative ions under the experimental conditions mentioned above. Corrected for the effects of the interpenetrating fields[2, 8] the mobilities in terms of the old accepted air standard of 1.4 and 1.8 cm/sec per volt/cm, and on the new absolute scale come out in cm/sec per volt/cm as

+ions	−ions	
0.544	0.424	old scale
0.654	0.510	new absolute scale

The negative value obtained is lower than that of Wahlin[4] obtained at lower pressures with undefined conditions of auxiliary field strength, and about of the order observed by Mayer's confessedly uncertain values at 8 cm pressure.[9]

The Work in Mixtures of Cl_2 and Air

In spite of Mayer's work on the air mixtures from 1 to 4.5 percent Cl_2, it was considered worthwhile to extend measurements in the mixture to higher concentrations using the pure Cl_2. To study the effects of mixtures of dry air and Cl_2 the following set of values were observed for a field strength fron 30-40 volts for bringing ions across, and an auxiliary field of 10 volts/cm. The uncorrected values were used to give the comparison of the mobilities with those computed from the law of mixtures of Blanc,[10] using the reciprocals of the mobilities instead of the mobilities as is the custom in the more recent work.[1]

Table III. *Mobilities in mixtures of Cl_2 and air.*

Mol fraction f of Cl_2	Mobility constants $K+$	$K-$	Mol fraction f of Cl_2	Mobility constants $K+$	$K-$
1.00	0.604	0.471	0.0011	1.61	1.46
0.427	0.905	0.676	0.0003	1.40	1.34
0.238	1.13	0.838	0.0001	1.48	1.48
0.119	1.25	0.91	trace	1.63	1.74
0.052	1.53	1.19	0.0000	1.61	2.00
0.025	1.51	1.20			

If the reciprocal of the mobility be written $R_f = 1/K_f$ (virtually the resistance to motion of the ion), then in a mixture containing a mol fraction f of Cl_2, the reciprocal of the mobility according to Blanc's[10] law should be given by

$$R_f = fR_{Cl_2} + (1-f)R_{air},$$

[9] Herbert Mayer, Phys. Zeits. **27,** 513 (1926) and **28,** 637 (1926).
[10] A. Blanc, Jour. Physique **7,** 825 (1908).

where R_{Cl_2} and R_{air}, are computed from the observations above, using the data actually observed for an auxiliary field of 10 volts/cm and an alternating field of 30-40 volts. The results are thus merely relative and not absolute, but could be reduced to absolute values by using the appropriate factors given in the reduction of the observed mobility in Cl_2 to the absolute scale.

The results observed are shown by the experimental points as crosses for positive ions and circled points for negative ions joined by the dashed lines in Figure 2. The full straight lines are computed from the Blanc's law above for this mixture and appropriately labelled as to sign.

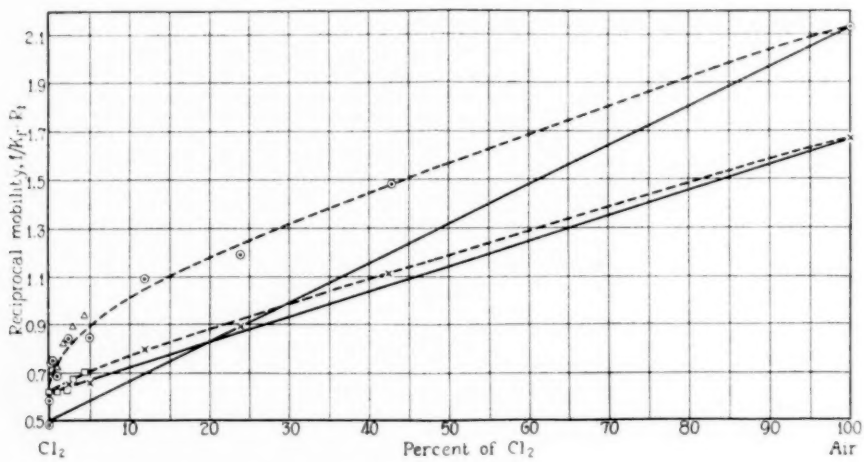

Fig. 2. Reciprocal of mobility as function of concentration of Cl_2 in a Cl_2-air mixture.

The early measurements of Mayer[9] from 1 to 4.5 percent Cl_2 are indicated by the triangles for negative ions and squares for positive ions. The positive observations of Mayer were multiplied by a factor to make Mayer's low positive values in air and air-Cl_2 mixtures coincide with the writers' for pure air. The reason for Mayer's low positive values in air lies in the fact that Mayer's apparatus due to lack of experimental facilities contained impurities which gave him a low positive mobility in air compared to negative values, (i.e. some organic vapors from his ebonite insulators). It is seen that Mayer's points for the negative ions agree remarkably well with the writers, considering the differences in technique used, and that on reduction to the same scale Mayer's positive ions show the same relative change in mobility as the writer's within experimental uncertainty.

Discussion

It is seen at once that the positive mobilities lie along the Blanc's law curve within the limits of experimental accuracy. This indicates that the *positive ions do not react specifically with Cl_2 molecules to form clusters.* As the dielectric constant of Cl_2 is low the effect of dielectric attractions observed in gases like HCl, SO_2 and NH_3[1,7] are absent as shown by agreement with

Blanc's law. It is further seen that the *negative ions have mobilities which drop from values of 2.00 to about 1.4 cm/sec for concentrations less than 1/2 of one percent.* The negative ions suffer therefore a very large, (perhaps the largest), decrease of mobility observed for additions of traces of any active gases to gases like air. This means not only a *specific cluster formation of Cl_2 about the negative ions but also a large cluster and a stable one.* It is also clear that this is due to some electrochemical affinity which is not caused by a high dielectric constant, for that of Cl_2 is low.

According to Blanc's law for Cl_2 the positive and negative ions should have equal mobilities at about 20 percent. This is also the value at which the positive and negative mobilities were *observed* to be equal for HCl. In these experiments traces of Cl_2 too small to measure made the mobilities of positive and negative ions equal. In Mayer's results as observed, due to an abnormal lowering of Mayer's positive mobilities by other impurities, the two mobilities were found equal at about 1 percent. This result as Mayer[9] has already pointed out indicates that the lowering of the negative mobility in his experiments was not due to HCl. The writer's work confirms this conclusion further by the use of Cl_2 free from HCl.

No trace of the capricious high positive mobilities with traces of Cl_2 were observed in the later experiments of the writer, even with the absence of the liquid air trap near the diffusion pump, and with the use of hydrogen as in earlier work. This may indicate that such results as mentioned earlier in this paper for Cl_2 and possibly also for SO_2[2] were due to imperfect electrical contacts in these reactive gases. In any case they were not reproduced in the present work and their uncontrollable appearance must be taken as an indication that they are spurious, and to be regarded with caution.

Conclusions

The conclusions to be drawn from these results are as follows: (1) The high irregular positive mobilities mentioned elsewhere in SO_2[2] and found in preliminary work in Cl_2 appear to be of a spurious origin, and must not be regarded seriously. (2) Cl_2 has no effect on the positive ion other than that predicted by Blanc's law and the mobility of this ion varies in Cl_2-air mixtures in much the same fashion as in H_2[2]-air or CO_2-air mixtures. There is no indication of a stable large cluster formation about the positive ion in Cl_2 and no indication of the effect of a high dielectric constant, as is to be expected as Cl_2 is said to be non-polar. (3) The negative ion shows a marked affinity for Cl_2 molecules. Cl_2 obviously forms a large and stable cluster about the negative ion even when present in minute traces. (4) The lowering of the mobility of the negative ion below that of the positive ion for traces of Cl_2 *must be ascribed to this cluster formation, due to a totally unexplained electro-chemical mechanism. It cannot be accounted for by the existence of an unsymmetrical dipole of large moment in the Cl_2 molecule,* which is a viewpoint put forward by Condon and Loeb[6] to explain the decrease of the negative mobility below the positive mobility in the cases of HCl, SO_2, H_2O, H_2S and other substances. It is surprising that this type of action should occur with the *Cl_2 molecule* since this *molecule* appears to have satisfied the strongly electronegative tendency of the

Cl_2 atoms relative to its other physical reactions in its formation. The chemical reactivity of Cl_2 on the other hand is due to a low heat of dissociation, and supposedly not to other properties of the Cl_2 molecule. The action on the negative ion is presumably analogous to the action of ethyl ether or NH_3 on the positive ions, yet how and why it takes place is in no sense clear.

With this work the writer is closing his investigation of mobilities in mixtures using the methods in which the mobilities of *unknown carriers are determined in gases where the carriers make* 10^7 *or more impacts with neutral gas molecules in the time of measurement.* In such cases purities of substances are required that are beyond chemical control. It is hoped that a new method which is being developed will enable the mobilities of ions of a known nature to be studied under conditions where impurities do not play the important role which they play in the usual measurements.

In concluding the writer desires to express his sincere thanks to his colleague Professor J. H. Hildebrand for his valuable advice in solving some of the many chemical difficulties encountered, to Miss L. DuSault who cooperated in the earlier measurements, and finally to his friend and research assistant Commander T. Lucci, late of the Italian Navy for his untiring assistance in the tedious work of preparation of and measurements in pure Cl_2.

ON MECHANICAL AND MAGNETIC FACTORS INFLUENCING THE ORIENTATION AND PERFECTION OF BISMUTH SINGLE-CRYSTALS

By Alexander Goetz
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(Received December 12, 1929)

Abstract

Method of producing crystals of bismuth.—A method is described which permits the production of single crystals of metals, with practically no limit to size or to desired orientation, thus indicating that all external mechanical influences are avoided. Furthermore, the method permits the zone of formation in a growing crystal to be subjected to a strong magnetic field.

Mechanical factors influencing the orientation and perfection of crystals.—A systematic study of the conditions in which the seed-crystal transfers its orientation to the rod is made. Experiments with artificially distorted seeds, etc., show that crystalline units must already exist in the liquid state. It is shown that this "liquid crystal" is destroyed at about 10° above the melting point. It is suggested that these units are identical with elementary units of a crystal as treated theoretically by Zwicky and observed by the author.

The influence of a magnetic field on a forming crystal.—Crystals in the three main orientations to the directions of the field lines (20,000 Gauss) were grown, one-half with, the other half without field. No change in the orientation between both halves could be observed as long as no secondary influence was present. However, crystals grown without a predetermined orientation indicated a preference for an orientation in which the direction of the smallest diamagnetic susceptibility (along the trigonal axis) was parallel to the lines of force. The fact that this influence, though much smaller than the orienting forces of a seed, exists, supports the assumption of "block-phase" slightly above the melting point.

Introduction

THERE are several reasons why a systematic investigation of the factors influencing the orientation and perfection of a metal crystal seems to be important. One of these reasons is the fact that certain methods of growing crystals succeed only for certain orientations, though the orientation is forced on the growing crystal by inoculation with a seed-crystal. Then it can happen that the desired orientation is only maintained over a short region or does not even start. In a previous paper,[1] Goetz and Hasler came to the same conclusion as Kapitza:[2] namely, that a growing crystal is very sensitive to any mechanical stress. Such stresses exist in almost every known method of crystal production. This necessitates the development of a new method which allows also the decision to be made as to whether this extremely sensitive region is in the solid part of the growing crystal or in the still liquid state.

[1] A. Goetz and Maurice F. Hasler, Proc. Nat. Acad. **15**, 646 (1929).
[2] P. Kapitza, Proc. Royal Soc. **A119**, 358 (1928).

Furthermore, it seemed to be interesting to see if directional forces of other than mechanical or thermal, especially magnetic, nature would show any influence when applied to the zone of formation. In spite of several papers written on this subject, no investigations excluding secondary effects have been systematically made. The results correlated from these papers contradict each other to some extent also.

The Method of Producing Crystals

After investigating the conditions for an unrestricted growth of Bi crystals by means of all known methods, it was found that these conditions can be summarized as follows:

(1) No strain of any kind should be applied to the zone of formation of the growing crystal.

(2) The crystal should not have any oxide-coat which can be the cause of stress.

(3) The speed of growth should be uniform.

(4) The heat gradient over the crystal should be uniform and its position within the crystal constant over the whole length.

(5) If the orientation of the crystal is to be predetermined by inoculation, it is necessary to obtain thermal equilibrium at the transition between seed-crystal and inoculated metal.

There is no method known which fulfills all these conditions equally well. However Kapitza's method, with which he produced the crystals finally used for his measurements, comes nearest, but it cannot be used for long crystals and does not satisfy condition (2).

Condition (1) seemed to me the most important one, and a large number of experiments were performed to fulfill it satisfactorily. One of the main troubles was that the molten metal (as soon as it was free from oxide) stuck to the walls of the container, thus interfering with the change of volume at crystallization. Many different arrangements were tried. For instance, a trough of thin paper was made in which the molten Bi was poured. When heated the paper carbonized, yet kept its shape sufficiently until the metal crystallized. The strength of these troughs was so small that the crystallizing metal could break them easily. Very uniform crystals were obtained by this method but the external shape was quite irregular. Finally, it was found that smooth troughs of Acheson graphite worked as well as the troughs of carbonized paper without having the disadvantage of losing their shape after the crystallization of the metal.

The final arrangement based on the previous experiences was the following: The troughs were shaped out of large blocks of Acheson graphite from a region free from fissures. The troughs had a length of 30 cm, were 0.4 cm wide and shaped rectangularly. Special precautions had to be observed in shaping to avoid deformations caused by the flexibility of the material. To fulfill condition (2) it was necessary to place the trough G in a glass or quartz tube C (in Fig. 1) which had at one end a ground-glass cone in which a little glass dome with a capillary was fitted. The cross-section of C was circular

over the whole length to within 3 cm of the cone, where it was as shown in the cross section (Fig. 1) elliptical to give more space above the trough. *F* was an electric furnace (chromel wire coiled around a quartz-tube) with two end plates, through the holes of which went the tube *C*, in such a manner that it did not touch the walls. The tube was supported at one end by means of the V-shaped adjustable holder *A* in which the tube glided over graphite wedges. The other end of the tube was supported at the clamp *O* which was a part of the driving arrangement fulfilling condition (3) (not shown in Fig. 1, because its design has already been published[1].) The connection between *O* and *C* was made with a rubber-tube *N* which absorbed to some extent the vibrations of the motor.

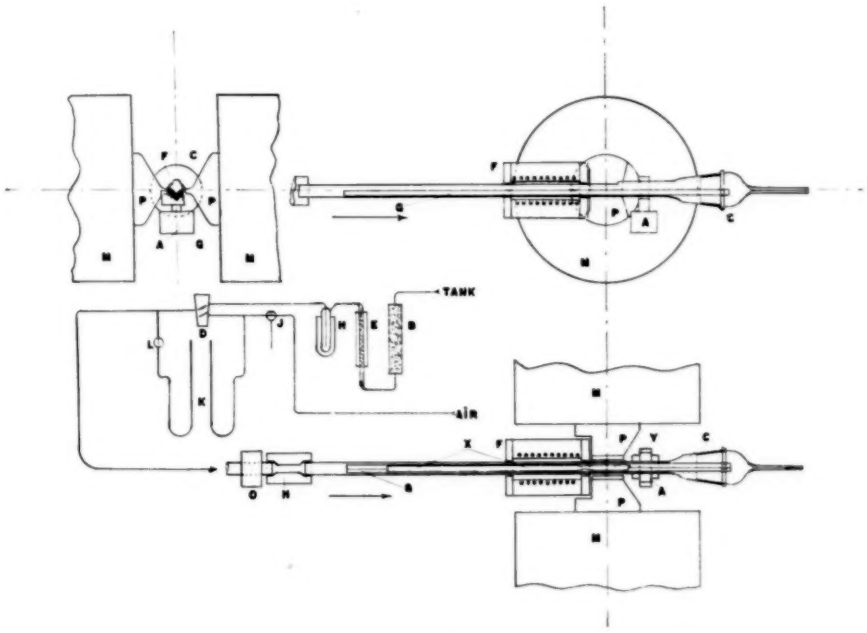

Fig. 1. Diagram of essential features of the apparatus.

The method of producing crystals was as follows: Round metal rods of 2–3 mm diameter were first made in glass tubes as described in another paper.[1] After the glass was taken off, the rods were cut down to a standard length of 120 mm (first generation).

The clamp *O* was then disengaged from the driving mechanism and moved towards the right so that the tube *C*, and with it the trough *G*, came out of the furnace *F* as far as possible. The glass dome was then removed and the rod placed in the trough. Then the tube was closed and the clamp *O* was put back into such a position that the end of the rod came out of the furnace *F* for a short distance. The furnace was restrictively heated so as not to melt the end of the rod. After the tube had come to thermal equilibrium with the furnace, the clamp *O* was engaged with the driving apparatus which moved

it in the direction of the arrow at a rate of 5 mm/min. To reduce the oxide at the surface of the rod a constant flow of hydrogen was sent through the tube. It soon became apparent that the purity of the hydrogen and the constancy of the flow were of great importance for the uniformity of the crystals, which made a rather elaborate arrangement necessary. The hydrogen was first taken from a tank with a reduction valve. To separate dust from the gas, it was then sent through a gas filter *B* and then through a heated tube with palladiumized asbestos to oxidize the impurities; thereafter through the trap *II*, cooled by liquid air, and then through the valve *D*. From here it went into the tube, over the metal and escaped through the capillary in the dome. The rate of flow could be measured by one of the manometers *K*.

By this arrangement, it was possible to keep the thickness of the oxide coat over the whole length of the crystal practically constant, since the factors determining the rate of reduction, temperature (very important), flow of hydrogen, and speed of the trough through the furnace could all be controlled. It soon became apparent that a perfect reduction is highly undesirable, because as soon as the last surface layer is gone, the surface tension of the liquid metal becomes so large that it coagulates into large drops and thus destroys entirely the uniform cross-section of the crystal. This effect made it necessary to provide an arrangement which permitted the production of a very thin oxide layer over the crystal. For this purpose, compressed air was used, which went first through the valve *D*, then through the stopcock *D* which opened the way to *C* either for the hydrogen or the air. For making the change between these two gases as fast as possible, every unnecessary apparatus-volume not exposed to the direct flow was avoided. Therefore, the hydrogen manometer, for instance, could be closed with the stopcock *L* as soon as the air-flow, which was measured by the manometer *K* (right), started.

For producing the "second generation," the rod was placed in the trough, as mentioned above, and the furnace heated to about 310°. To prevent coagulation, the first few millimeters were placed so that they did not melt, then the hydrogen flow was turned on at a pressure of 20–25 mm water-column and the motor started. Thus the metal rod melted into the shape of the trough and was reduced so that the surface became very bright. As soon as the other end of the rod entered the furnace the hydrogen-flow was stopped and the air-flow started to cover this part with an almost invisible coat which fixed the shape of the end of the rod and thus prevented the metal from running forward under the influence of surface tension.

This second generation was, in general, monocrystalline, but the orientation was at random. To predetermine the orientation the method of inoculation by a seed-crystal was used. For this purpose, the metal rod obtained by the previous methods was placed again in the trough, the latter being placed in the furnace, again under a flow of hydrogen, so as to melt the right end of the rod. The thin oxide-coat kept the end in shape, since the temperature (about 290°) of the furnace was so low that no appreciable reduction occurred. As soon as the end was liquid (Fig. 2a), the glass dome of *C*

was removed, a hooked steel needle was introduced and the oxide coat taken off the end of the liquid rod (Fig. 2b). The hydrogen flow prevented a re-oxidation of this point, whereas the oxide-hull of the rest kept the rod in shape. Then the seed-crystal, the end of which was cleaved immediately before using, was brought into the trough (Fig. 2c). The liquid end of X and the left end of Y were brought into contact very carefully, so that they united over a small region (Fig. 2d). Again coagulation had to be avoided by pulling the seed-crystal out a trifle so as to produce a little constriction between X and Y. (Fig. 2e). The glass dome of C was then replaced, the tube itself pushed back into the furnace for annealing the transition (Fig. 2f) and the hydrogen-flow was replaced by an air-flow. This process was necessary in order to protect the very delicate junction between X and Y by a uniform oxide coat (see later). After the rod and the seed-crystal reached

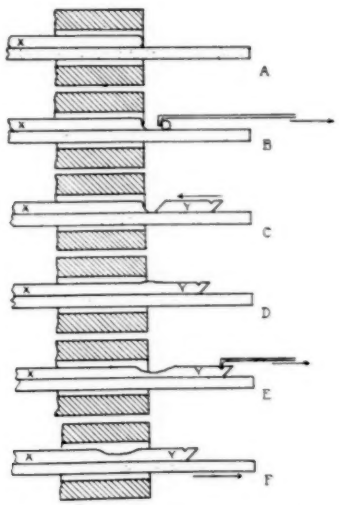

Fig. 2. Method of inoculating rod with seed crystal.

thermal equilibrium, corresponding to the new position in the furnace, the motor was started and thus the crystal started to grow. As soon as the junction came out of the furnace, the air flow was replaced by hydrogen to prevent a thickening of the oxide coat on X. It was found that this oxide coat had to be very thin, almost invisible to the eye, and had to be very uniform over the whole rod. For fulfilling this condition, it was necessary to start the hydrogen rather exactly at the moment at which the junction started to crystallize. The moment at which the air inside C was replaced by hydrogen could easily be observed on account of the difference of viscosity of the two gases. The storage pressure of the hydrogen indicated by the manometer K (left) was large as long as the rest of the air had to flow through the capillary of C, but went down to a constant value as soon as the tube contained only hydrogen. The opposite was the case if the hydrogen was replaced by air.

Thus the third generation of the crystal was obtained. After the whole rod crystallized, it was taken out of the trough very carefully and etched with diluted nitric acid. If all precautions had been observed carefully, the crystal obtained was perfectly uniform in shape and orientation, and not the smallest alien crystal could be observed. The orientation of the crystal was

Fig. 3. Crystal 1 shows first "generation" after removing the glass cover. It is polycrystalline and shows many regions of twinning. Crystal 2 is second "generation," its core being singly-crystalline. However, its surface contains many crystals in twin orientations due to oxide stress. Crystal 3 is third "generation" (X) with the seed-crystal (Y) in orientation P_1. The rod is a single crystal.

exactly the one of the seed crystal, no matter which orientation that had. It was found also that this method had no limitations in the matters of the lengths and the cross-sections of the crystal. Fig. 3 shows a photograph of the first three generations of crystals.

As has been mentioned above, the whole investigation was undertaken to study the factors influencing the orientation and perfection of these

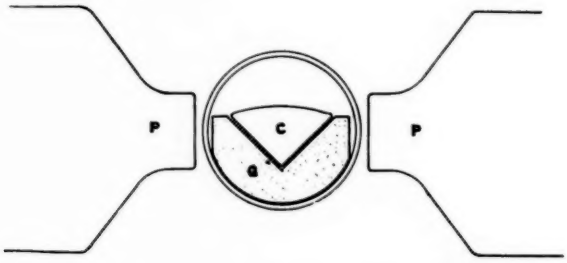

Fig. 4. Cross-section of arrangement for crystallization in a magnetic field.

crystals with special regard to the influence of a transverse magnetic field. The method just described allowed a very exact location of the zone in which the crystal formed. If the temperature of the furnace was high enough, this zone was outside the furnace; hence it was possible to bring it between the pole-pieces of an electromagnet M. The pole-pieces P were shaped so as to concentrate the field between two edges and thus across the crystal over a

length of 18 mm. This distance was necessary to allow for the unavoidable uncertainty in the exact position of the zone of formation. Fig. 4 shows an enlarged cross-section of the arrangement whereas Fig. 5 is a top view photograph which shows the crystal *C* lying in the trough *G* as it comes out of the furnace *F* and crystallizes between the pole pieces *P* of the magnet *M*.

This method has the disadvantage that the direction of the lines of force cannot be changed relative to the rod. Nevertheless, it is possible to change the orientation in the rod by inoculation with different seed crystals. This allowed the study of the influence of the field at different angles with regard to the trigonal axis.

Fig. 5. Top view of the formation of the single crystal *C* carried in the trough *G* between the pole pieces *PP* of the magnet *M* after being molten in the furance *F*.

Mechanical Factors Influencing the Orientation and Perfection of Crystals

For studying the kinds of influences preventing a perfect growth of Bi-crystals, about 500 crystals were grown under circumstances which were changed systematically. The results concerning the disturbances involved in the artificial growth by inoculation can be summarized as follows.

Two different kinds of mischief in the production of single crystals have to be separated, (a) the fact that the rod consists of several crystals with different orientations, and (b) the fact that the inoculation of the rod by a seed-crystal does not succeed. All experiments were performed at a constant speed (exact to about 0.2 percent), in absence of vibration, and at a constant temperature (exact to 2°).

The failure of an inoculation can consist of

(1) That the orientation of the rod has no relation whatsoever to the seed crystal;

(2) That the orientation of the rod is partly the same as the seed crystal;

(3) That the orientation of the rod is the twin orientation of the seed crystal.

The first case occurred in general if the contact between rod and crystal was bad. It was quite remarkable how an almost invisible layer of oxide between both parts destroyed entirely the influence of the seed crystal,

although they may have congealed and formed a unit after solidification. Case (2) can have the same cause as (1). If the face of contact between both parts was partly contaminated by oxide, then one half grew in the orientation of the seed crystal, whereas the other half, separated from the seed by contamination, formed one or several new centers of crystallization which produced new crystals which grew together with the inoculated one. There may be still another cause which will be discussed later. The most interesting case is (3). Here one can have a perfect crystal, the orientation of which is the same throughout, only that the perfect cleavage of the seed plane is replaced by one of the imperfect cleavage planes. The same effect may occur in case (2), where one can obtain the parallel growth of two crystals with interchanged planes.

It is well known that almost any deformation in a Bi crystal results in the production of twin-lamellae[3,4] where the (111) plane is replaced by one of

Fig. 6.

Fig. 7.

Twin lamellae caused by distortion in Bi single crystals. The illumination under the microscope was such as to show the original orientation of the crystal dark (Fig. 7) or bright (Fig. 6). The white line in Fig. 7 corresponds to 1 mm.

the $(11\bar{1})$ type. The change takes very little energy because the rhombohedral symmetry of Bi is almost a cubic one. Fig. 6 and Fig. 7 illustrate this effect on two artificially distorted crystals of Bi, which show the appearance of the twin lamellae differently illuminated. Thus the conclusion is easily reached that the twinning occurred in case (3) at the point where seed and rod came in contact. A close investigation of this effect brought out the following facts.

If the seed-crystal is not perfect, i. e. if it contains twin lamellae which are easily observed under the microscope after etching (3) the rod will grow frequently in the twin orientation. It is furthermore very hard to avoid the twinning effect if one cleaves crystals in special orientations, as was shown by x-ray diagrams, but it is possible by careful handling to extend the twinned region not farther than a few tenths of a mm beyond the cleaved plane. Thus

[3] P. Mügge, Jahrbuch d. Mineralogie **1**, 183 (1886).

[4] A. Goetz, Proc. Nat. Acad. in press.

in order to inoculate the rod with an undisturbed seed, it is only necessary to bring the trough, after the contact between rod and seed is made (Fig. 2 e) far enough into the furnace so that the imperfect end of the seed is melted (Fig. 2 f). Then the unhurt part of the seed reinoculates its imperfect part and the rod starts to crystallize in the desired orientation.

However, it was very surprising that case (3) occurred very often, even though this precaution was taken, i.e. the rod crystallized in the twin orientation in spite of a perfect seed.

Closer investigation showed that this effect had two reasons. One should expect that if one inoculates with well twinned seed crystals i.e. where distinct regions of the crystal have either the normal or the twin orientation as shown in Fig. 6 and 7, one would obtain rods of both orientations depending on the position of the point up to which the seed was melted. But it was discovered that *the rod grows in an orientation possessed by a region of the seed which was already molten*. This process is shown schematically in Fig. 8 where X is the molten rod and Y the seed crystal having the twin-lamellae $t, t \ldots$. In case the seed Y was molten up to point 1, X grew in the orientation corresponding to the seed. If Y was molten up to point 2, X grew in the twin orien-

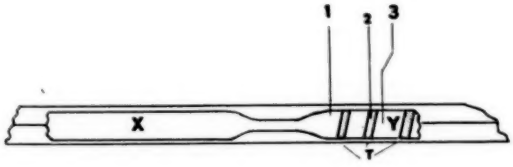

Fig. 8.

tation. But if Y was liquidified up to point 3, where the twin lamella was doubtlessly melted, X grew still in the twin orientation. This experiment could be repeated as often as desired. The maximum distance still effective between the border of the lamella and the end of the molten region was, in general, several millimeters. Fig. 9 shows an enlarged photograph of the transition between seed and rod. The illumination of the crystal is such as to show the parts of the desired orientation bright. The dark crystal is the seed (right) which shows three good intersections of twin lamellae. The white half to the left is the beginning of the inoculated rod, which shows the same orientation as the twin lamellae of the seed-crystal. The sharp transition shows how far the seed was melted. The original end of the seed had one twin lamella which was melted about 0.5 mm beyond its left border, but was still able to determine the orientation of the rod. The faint black lines on the left crystal are twin lamellae in the rod which were produced later to show that they have the original orientation of the seed indicated by their dark appearance.

This phenomenon shows that the forces determining the orientation of a crystal are not destroyed at the melting point and exist within the liquid as long as the temperature is near to that of the melting point.

The study of the conditions of successful inoculation with untwinned crystals (or seeds melted far beyond the limits of the imperfections) revealed

another phenomenon which points in the same direction. As mentioned above it was necessary (to preserve the perfect shape of the rod) to pull the seed a little away from the rod (Fig. 2 d) so that the junction was constricted (Fig. 2 e). It goes without saying that this constriction concerned only the region where the metal was molten entirely. It was found, nevertheless, in almost all cases, that the rod grew in the twin orientation of the seed if the crystallization was started from the position of the trough in Fig. 2 e. After the crystal was finished, it was etched and the region where the twin orientation occurred could be determined easily. It started aways close to point 1 (Fig. 4 e) i.e. at the beginning of the constriction, no matter whether the melted region of the seed reached still farther or not.

The only way to avoid this twinning effect in the liquid was to anneal the liquid junction at temperatures much higher than the melting point; hence the

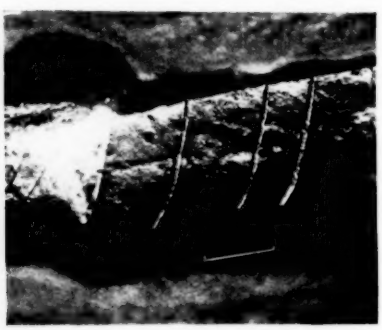

Fig. 9. Seed crystal with twin lamellae (right), inoculated crystal (left) grew in twin orientation although the twinned region of the seed was molten. The white line corresponds to 1 mm.

trough had to be backed into the furnace (Fig. 2 f) and kept in that position for 5-7 minutes before the crystallization was started.

This effect shows that within the temperature region of the "liquid crystal," the twinning occurs just as well as in the solid state with the only difference that the little energy necessary for changing the shape of the liquid rod (determined by its surface tension and the shape of the thin oxide cover) is already sufficient to produce the effect.

The fact that the orientation of a crystal is not destroyed immediately after melting could be shown in another experiment. If a polycrystalline rod (first generation) was put into the trough and was run throught he furnace with the usual speed, but a maximum temperature which was only slightly above the melting point, a polycrystalline rod was obtained which had the same position and the same orientation of the different prominent crystal elements as it had before it entered the furnace although it had been molten and recrystallized. As soon as the temperature was higher, an entirely different polycrystalline combination occurred.

The high sensitivity to any stress applied to the transition between solid and liquid metal causes another effect which is highly undesirable. If a single crystal rod which is covered by oxide was placed in the trough and pulled through the furnace, a rod was generally obtained which was monocrystalline at the core but polycrystalline at the surface, an observation which was also made by Kapitza[2]. Under the microscope, it was observed that the alien crystals have the shape of thin stripes running along the rod, each of them starting at a wrinkle in the oxide coat produced by the shrinking of the metal at the moment of melting. As soon as the rod crystallizad, these wrinkles were stretched out again, but the pressure necessary for this process was sufficient to cause twinning if the oxide coat was sufficiently thick. The alien crystals produced by this cause were only at the surface and could be removed by etching. The effect was different if the rod was free from oxide and the oxide coat was produced around the rod in the molten state. Then the whole hull was too small for the solid form and it had to be split by the solidifying metal, which caused pressures which were very often able to start an entirely new orientation. Hence it was necessary to grow the metal in a reducing atmosphere so that the oxide coat was too thin to affect the structure of the crystal, but sufficient to preserve the shape of the molten rod.

With regard to the orientation which is produced by these stresses, the following can be said: Any tension longitudinal with regard to the rod results in an orientation in which the trigonal axis is normal to the rod. If the original orientation is already such, the tension has no influence at all. If the stresses are not very large, the new orientation is obtained by twinning which places the trigonal axis in a direction in which the energy needed for overcoming the obstacles of thermal contraction is smaller. This is the reason as already stated in another paper,[1] crystals, the trigonal axes of which are parallel to the rods, are very difficult to obtain with the usual methods, which apply either longitudinal tensions or lateral compressions to the zone of formation due to the expansion of the metal at the moment of crystallization. The method described avoids these influences and allows the growth of all possible orientations equally well. However, the opposite effect can be shown, where a longitudinal compression prevents the perfect growth of a crystal, the axis of which is normal to the rod. If a rod was covered with a heavy oxide coat and inoculated with a seed, the axis of which was normal to the rod, the last end of the rod had an orientation in which the axis became more parallel to the rod. The obvious reason is that the oxide at the end of the rod formed a kind of sack, the end of which prevented the longitudinal expansion and thus exerted a longitudinal compression, which resulted in an orientation of maximum contraction parallel to it.

The Influence of the Magnetic Field Upon the Crystallization.

Since the orientation and perfection of these crystals could be influenced mechanically when in the molten state, it seemed worth while to study whether or not a magnetic field applied to the zone of formation would produce any effects.

The way in which the magnetic field was applied has already been described. The tests were made as follows: The crystal (third generation), with an already definite orientation, was put into the trough and the tube pulled back into the furnace so far that the left end of the crystal did not melt. The temperature of the furnace was increased so much that the transition between liquid and solid crystal was approximately at the middle of the pole pieces when the crystal reached its thermal equilibrium, a process which took in general, 5 minutes. Then the magnetic field was excited and the driving mechanism started at the same time. Thus the molten part of the rod crystallized again within a transversal magnetic field of a strength of 20,000-21,000 gauss.

It is obvious that there are three different possible orientations of the crystal with respect to the rod, or to the direction of the lines of force. These orientations which differ fundamentally are as sketched in Fig. 10. This

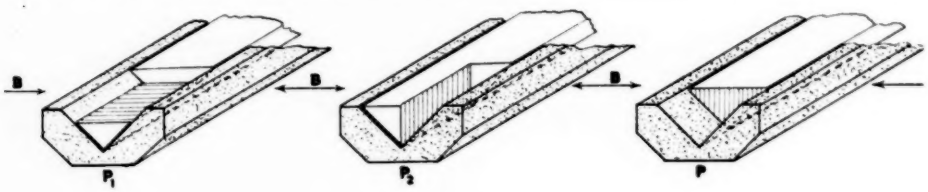

Fig. 10.

shows the trough G (dotted) with the crystal, the latter cut parallel to its main cleavage plane. These three main orientations are:

Name	Trigonal axis to rod	Trigonal axis to field	(111) plane to rod	(111) plane to field
P_1	$\perp$	$\perp$	$\parallel$	$\parallel$
P_2	$\perp$	$\parallel$	$\parallel$	$\perp$
P_3	$\parallel$	$\perp$	$\perp$	$\parallel$

As long as the conditions of growth were not influenced accidentally, *no influence of the magnetic field upon the crystallographic orientation could be observed, no matter which of the above main orientations was introduced into the field.* It is to be mentioned however, that this result can only be obtained if one succeeds in avoiding any secondary influence. Any shock, for instance caused by the sudden excitation of the magnet, transferred to the trough or to the furnace will immediately produce a change in orientation.

Moreover, crystals, the orientation of which had not been predetermined, were grown in a magnetic field to find out whether there exists an influence of the field on the first originating center of crystallization. In fact, indications were found which point toward a preference of an approximate parallelism of the trigonal axis and the lines of force. However, these results seem not to be precise enough for a definite statement, since first the number of measured crystals produced this way was not large enough that the results could be considered statistically; and second, it is known that the direction of the

heat-gradient with relation to the rod can predetermine the orientation aside from any mechanical influence. Thus, the non-inoculated crystal may not have been entirely free to grow in any orientation because the apparatus did not allow a change of the direction of the heat-gradient with respect to the rod. On the other hand, it is certain that these predetermining influences are extremely small because they cannot affect, in any way, the growth of an inoculated crystal. However, the influence of the applied field showed itself to be smaller than the orienting forces of an inoculating crystal and may be similar in magnitude to the orienting forces of the gradient, which makes it possible that the effects produced by the latter fog the former.

Discussion

The results obtained by the above observations may be able to explain a number of experiences of other authors. It has been already suggested in a previous paper[1] that the extended experiments of Hoyem and Tyndall[5] on single zinc crystals may find their explanations in the effect of the stress applied to the zone of formation by the weight of the liquid column hanging from the crystal. The variation of the successfulness of an inoculation with the temperature of the molten metal can thus be explained, because the length of the liquid column depends upon that temperature and herewith its weight.

Moreover the lack of success of several methods of Kapitza[2] and his explanation thereof is confirmed and becomes understandable as soon as one realizes that in the case of liquid bismuth, the interchange of the main cleavage plane with an $(11\bar{1})$ plane is exactly the effect which occurs in any plastic deformation of solid bismuth. It seems that there are only two alternate interpretations possible: First, one could assume that the twinning force of the crystal becomes infinitely small in the neighborhood of the melting point so that the smallest strain, as given, for instance, by the surface tension of the liquid metal, is sufficient to start the twinning; or second, in view of the observed facts one might assume that the twinning effect occurs within the melted region, which would mean that the crystal is not destroyed entirely after melting, but that it consists still of units which preserve their orienting power. The first makes it impossible to explain the fact that qualities can be "inherited" by a growing crystal from the molten region of a seed crystal or to explain the preservation of a polycrystalline structure in a bar heated above the melting point. These units exist apparently only over a small range of temperature, since the phenomena through which one infers their presence disappear entirely about 10° above the melting point (annealing of the liquid metal).

One is perhaps not entirely wrong in assuming that these units are of the of the same nature as the "blocks" in a Bi-crystal described by the author in a recent paper[1] in connection with the theoretical considerations of Zwicky.[6] In this case, one considers that the melting crystal disintegrates first into its

[5] A. G. Hoyem and E. P. T. Tyndall, Phys. Rev. **33,** 81 (1929).
[6] F. Zwicky, Proc. Nat. Acad. **15,** 253, 000 (1929).

blocks which exist within a state of equilibrium of dissociation with the liquid metal at each temperature. This "block phase," however, exists only over a small range of temperature.

There are several indications in experiments of other authors which are in favor of this hypothesis. Boydston[7] found in observing the thermal e.m.f. of Bi-crystals of different orientations that the e.m.f's characteristic for the crystalline state did not disappear exactly at the melting point, but continued for a few degrees. Thus (to quote his own words) "it appears, in fact, as if some crystalline arrangement still persists in the molten metal . . . ."

Futhermore, Traube and vonBehren have shown[8] that the dissolving of a crystal into an almost saturated solution results in separating particles of ultra-microscopic size from the crystal, "submicrons," which exist for a considerable length of time. The parallelism between the melting process and the process of dissolving into a saturated solution does not need to be mentioned.

Finally, it is possible to connect the observations by Stewart and his collaborators[9] concerning the "cybotactic" state of matter with these results. It seems as if there is no principal difference between the "block-phase" and the "cybotaxis."

Regarding the extremely small energy needed for influencing the orientation in a liquid crystal, I was surprised to find no orientating effect caused by the magnetic field on a crystal with a predetermined orientation. This however, does not contradict necessarily, experiments which were performed by Plücker[10] and Leduc.[11] From experiments on polycrystalline Bi solidified in a magnetic field, Plücker finds that among the individual crystals, one direction is predominant, that is where the trigonal axis is parallel to the lines of force. A result of this kind should be expected, if there is any positive effect, because of the anisotropic diamagnetism of Bi, as the trigonal axis is known to be parallel to the most "paramagnetic" direction. The observations of Leduc[11] point in the same direction. He crystallized Bi in spherical glass containers which could be suspended within a field of 4-5000 Gauss. These Bi balls were polycrystalline without doubt, but suspended in the field they turned into a direction in which the "average main axis" of the conglomerate was parallel to the lines of force. If the ball was formed outside the field, no prediction about its zero position in the field could be made, but as soon as the sphere had crystallized within the field, the zero position was the same as its position during the crystallization. The explanation of this effect is obviously the same as of Plückers' observations, although, the orientation of the conglomerate was not measured by Leduc.

It seems surprising that Welo did not find any effect of this kind in a recent study.[12] It may be due to the fact that his way of casting his disk in a

[7] R. W. Boydston, Phys. Rev. **30,** 911 (1927).
[8] J. Traube and W. von Behren, Sx. f. Phys. Chem. **A138,** 85 (1928).
[9] G. W. Stewart and R. M. Morrow, Phys. Rev. **30,** 232 (1927).
[10] S. Plucker, Pogg. Ann. **76,** 583 (1849).
[11] M. A. Leduc, C. R. **140,** 1022 (1905).
[12] L. A. Welo, Phys. Rev. **34,** 296 (1929).

mould with good thermal conductivity produced a polycrystallization so rapid that the orienting effect was very small.

Our own observations make a directional effect, in a crystal which crystallizes completely in a magnetic field, probable with a sign which agrees with Plücker's and Leduc's experiments. They show, however, that this effect is so small that it cannot overcome the orienting forces of a seed-crystal.

The presence of the magnetic effect shows furthermore, that the orientation of a crystal must exist already in the liquid state provided that the crystal unit has still freedom to move with regard to the rod. This supports again the existence of the above "block-phase." The insensibility of the inoculated crystal shows further that the growing crystal, if under stable conditions, must have an already ordered section of the liquid ahead of it. Then the orienting effect of a magnetic field is too small to break up the liquid arrangement.

Nevertheless, it was found that the magnetic field influences considerably other properties of a Bi crystal formed in it, as stated already by the author and his collaborators[13, 14, 15]. More extensive results will be published soon.

I feel very much indebted to Dr. R. A. Millikan for the interest he showed in this investigation, and I should like to express my thanks to my assistants, Mr. M. F. Hasler and Mr. A. B. Focke for their very helpful assistance.

[13] A. Geotz, Phys. Rev. **32,** 322 (1928).
[14] A. Goetz and M. F. Hasler, Phys. Rev. **34,** 549 (1929).
[15] A. Geotz, R. C. Hergenrother and A. B. Focke, Phys. Rev. **34,** 546 (1929).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Hyperfine Structure in the Spectra of Neutral Manganese

A light source, designed by Schüler, operated at liquid air temperatures in conjunction with a prism spectrograph and silvered Fabry-Perot etalons is being used to study the hyperfine structures in the spectral lines of neutral manganese. At 4000Å a resolving power of approximately one million is obtained. The observed fine-structure patterns although identical in appearance with those found in praseodymium (Phys. Rev. **34,** 1397, 1929) are in general a fifth to a tenth as wide. Patterns of from 2 to 6 components are found, some degrading toward the red and others toward the violet. For example, λ4030 has the fine-structure components,

Int.	10	9	8	7
$\Delta\lambda$	0	+0.0122	+0.0230	+0.0317
$\Delta\nu$	0	−0.0751	−0.1416	−0.1951
			6	5
			+0.0379	+0.0420
			−0.2333	−0.2585

degrading toward longer wave-lengths while λ4018 has the

Int.	10	9	8	7
$\Delta\lambda$	0	−0.0152	−0.0274	−0.0377
$\Delta\nu$	0	+0.0941	+0.1696	+0.2333
			6	5
			−0.0456	−0.0516
			+0.2822	+0.3193

components degrading toward the violet. Since the well-known gross structure of Mn I and II in general shows strictly *LS* coupling, an excellent opportunity for the study of the role played by *s*, *p*, and *d* electrons in producing hyperfine structure presents itself. The ${}^6S_{2\frac{1}{2}}$ $(3d^5 4s^2)$ term is apparently quite narrow. With a nucleur angular momentum $(5/2)\,(h/2\pi)$ for Mn, the ${}^8P_{4\frac{1}{2}}$, ${}^6P_{3\frac{1}{2}}(3d^5 4s4p)$ and the ${}^6D_{4\frac{1}{2}}(3d^6 4s)$ terms are each broken into six *normal* components with separations 0.116, 0.107, 0.082, 0.068, 0.052 and 0.075, 0.066, 0.054, 0.038, 0.025, and 0.099, 0.086, 0.069, 0.054, 0.040 cm^{-1} respectively. While the ${}^8P_{4\frac{1}{2},3\frac{1}{2},2\frac{1}{2}}$ terms each have six components, the ${}^6D_{4\frac{1}{2},3\frac{1}{2},2\frac{1}{2},1\frac{1}{2},\frac{1}{2}}$ and ${}^6P_{3\frac{1}{2},2\frac{1}{2},1\frac{1}{2}}$ terms have 6, 6, 6, 4, 2 and 6, 6, 4 components respectively, as would be expected with $i=2\frac{1}{2}$. The total fine-structure separation 0.348 cm^{-1} for ${}^6D_{4\frac{1}{2}}$ $(3d^6 4s)$ is due chiefly to the $4s$ electron, the $3d$ electrons contributing very little. To this the $4p$ electron contribution is (a) added to give the ${}^8P_{4\frac{1}{2}}(3d^5 4s4p)$ separation 0.414 cm^{-1} and (b) subtracted to give the ${}^6P_{3\frac{1}{2}}(3d^5 4s4p)$ separation 0.258 cm^{-1}.

The total separations of the fine structures for the three terms ${}^6D_{4\frac{1}{2},3\frac{1}{2},2\frac{1}{2}}$ are found to be proportional to the cos si, when $J \geqq i$ and cos $Ji=1$, as predicted. The fine structures that have as yet been photographed are found to be in excellent agreement with the "Theoretical Interpretation of Hyperfine Structure" given by one of the authors (H. E. W. in a Letter to the Editor, Phys. Rev **34,** 1288, (1929). The value of i for manganese appears to be $(5/2)\,(h/2\pi)$ as is also the case for lanthanum and praseodymium. The ratio between gross-structure and fine-structure is about 20,000:1 the same order of magnitude as the ratio between the mass of a manganese atom and five times the mass of an electron. This indicates that if the nuclear spin is due to negative charges, as seems to be the case from the *normal* order of the fine structure, they must carry with them the total mass of the nucleus in space quantization.

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R. Ritschl

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December 7, 1929.

The Unified Field-Theory and Schwarzschild's Solution

Vallarta[1] has investigated, with negative results, the consistency of Einstein's unified field-theory with the generalized relativity theory of 1916 as regards the gravitational equations in a spherically symmetrical field. It appears, however, that he made a slip toward the beginning of his calculation. The expressions for the potentials should be

$$\phi_i = 2\Lambda x_i - \frac{W' x_i}{Wr} \qquad (i=1,2,3)$$

instead of simply the first term. As a result, Vallarta's expressions for $V_{\beta\gamma}{}^{\alpha}$ and $V^{\alpha\beta\gamma}$ are wrong. When the necessary corrections are applied, Vallarta's gravitational equations

$$\frac{\partial V^{\alpha\beta\gamma}}{\partial x_\gamma} + V^{\sigma\beta\gamma}\Gamma_{\gamma\sigma}{}^{\alpha} + V^{\alpha\sigma\gamma}\Gamma_{\sigma\gamma}{}^{\beta} + V^{\alpha\beta\sigma}\Gamma_{\gamma\sigma}{}^{\gamma} = 0 \qquad (1)$$

yield, for the case $\alpha=\beta=4$

$$dU/dr = U/r - U^2/r$$

where U is the square-root of the coefficient of dr^2 in the fundamental quadratic differential form. The solution of this differential equation,

$$U = \frac{1}{1-(m/r)},$$

where m is a constant, is identical with Schwarzschild's solution for the coefficient itself. The agreement extends, therefore, as far as the first power of m/r.

For the cases $\alpha=\beta=i$ $(i=1, 2, 3)$, one of the consequences to be deduced from (1) is the differential equation

$$W(U-1) - rW' = 0$$

where W is the square-root of the coefficient of dt^2 in the fundamental quadratic form. This is satisfied, though, of course, not uniquely, by a function identical with Schwarzschild's solution for the coefficient itself:

$$W = 1-(m/r),$$

the approximation being of the same order as in the case of U. It must be borne in mind however, that the implications of (1) have by no means been exhausted.

It would indeed be surprising, in view of the basic similarity between Vallarta's and Schwarzschild's metrical assumptions, and in view also of the relation between Einstein's theories of 1916 and 1929, were results wholly at variance with Schwarzschild's solution obtainable from Vallarta's problem.

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December 31, 1929.

[1] M. S. Vallarta, Proc. Nat. Acad. Sci. **15,** 784 (1929).

Limiting Resolving Power of a Crystal Grating

From time to time one sees in the literature reports of unsuccessful attempts to find certain fine structures in x-ray spectral lines. These attempts are generally made by the single crystal photographic method, but the following considerations apply to other spectrometers, either single or double crystal type.

The resolution is limited by the "tolerance" angle of the crystal. This "tolerance" angle, namely, possible deviations from Bragg's Law, is determined by the parallel crystal method on the double spectrometer. The crystals used by Davis and Purks (Proc. Nat. Acad. Sci. Feb. 1928) in analyzing the structure of the Mo$K\alpha_1$ line gave a rocking curve of 6 seconds at half-maximum, at first order. The corresponding width at second order would be 2″ of arc. The tolerance angle of one of these crystals was $6/2^{1/2}=4''$, at first order and $2/2^{1/2}=1.4''$ at second order.

The Bragg law of crystal reflection is $\lambda = 2d \sin\theta$, so $d\lambda = 2d\cos\theta d\theta$. The fine structure displacement is represented by $d\lambda$. In the case of the Mo$K\alpha_1$ fine structure the observed displacement was 0.085 x.u. This gives the angular displacement $d\theta = 3$ seconds of arc. This deviation is less than the tolerance angle of the best crystal at first order and of course the structure would be entirely washed out. Such fine structure is beyond the power of a single crystal analysis, no matter how great the distance between slits or the distance of the photographic plate.

The above applies also to double crystal analysis. Unless the tolerance angle at any order is less than the fine structure displacement, the structure will not be observed.

The width of rocking curve given here is for fine calcite. The corresponding curve for good rock-salt is 600 seconds (Davis and

Stempel, Phys. Rev. May, 1922). Rock-salt is of course not suited to fine structure work.

In general no crystal should be used for fine structure observation until its tolerance angle has been determined. Many specimens of calcite give quite wide rocking curves and are unsuited to this type of experiment.

BERGEN DAVIS

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January 4, 1930.

The Third Law of Thermodynamics

R. H. Fowler admits the practical utility of the concept of absolute entropy but maintains that no theoretical significance is to be attached to the concept. This viewpoint seems at variance with the one in vogue at the present time in physics.

If we treat absolute entropy as an operational concept the only question that needs to be considered in connection with the Third Law, is whether it is ever necessary to assume the entropy of the pure stable crystalline form of a substance different from zero at 0°K in order to calculate the correct value of the entropy from the thermal data. Difficulties might be anticipated in the case of elements in which the atoms have j values different from zero where it might prove necessary to add a term $R \ln (2j+1)$ to the value obtained from the thermal data. In the case of the sodium atom (Rodebush, Proc. Nat. Acad. **13,** 185 (1927)) and the oxygen molecule (Giauque and Johnstone, Jour. Am. Chem. Soc. **51,** 2300 (1929)) it has been shown that the thermal data alone lead to the correct value, so that apparently no correction factors are likely to be needed for electronic moments.

In the case of nuclear spins the situation is otherwise. Here theoretically the thermal data alone should still give the correct value of the entropy but practically only in the case of hydrogen (Rodebush, Proc. Nat. Acad. **15,** 678 (1929)) can the correct value of the entropy be obtained in the customary manner. For all hydrogen compounds we shall presumably have to add arbitrarily the quantity $R \ln 2$ per gram atom of hydrogen to the thermal entropy. In the case of other elements having nuclear spins the term $R \ln (2s+1)$ may be omitted from the entropy of elements and compounds alike for all thermodynamical calculations.

It is not to be doubted that in the case of an element such as sodium which has a nuclear spin of several half units, that a heat effect due to the change in orientation of the nuclear spins will appear at low temperatures, but the heat effect will be so small and the temperature so low that it will probably elude observation, although the corresponding entropy change is, of course, not negligible. The more or less prevalent idea that no appreciable entropy changes occur at very low temperatures is evidently not justified.

The only other case that needs to be noticed is that of elements which are isotopic mixtures. If we consider the separation of isotopes as a process which is realizable thermodynamically then we shall have to consider the isotopic mixture as a solution and solutions together with supercooled liquids are unstable forms of matter at 0°K and the Third Law does not apply to them.

W. H. RODEBUSH

University of Illinois,
December 23, 1929.

Note on Hartree's Method

Hartee's method of self-consistent fields, for determining atomic models, has seemed to many persons to stand rather apart from the main current of quantum theory; in spite of the papers of Gaunt and the writer, showing its connection with Schrödinger's equation, it has seemed to contain arbitrary and empirical elements. It appears, however, that it has a very close relation to the variation method. That principle states that, if one has an approximate wave function containing arbitrary parameters or arbitrary functions, one will have the best approximation to a solution of Schrödinger's equation if one chooses the parameters or functions so that the energy is stationary with respect to slight variations of them. Suppose one sets up an approximate wave function for a general problem of the motion of electrons among stationary nuclei, by assuming a product of functions of the various electrons: $u=u_1(x_1)\cdots u_n(x_n)$; suppose further that

one apply the variation principle by varying separately each of the functions u_i, leaving the others constant. The n variation equations so obtained prove to be those for the motion of the n electrons, each in a separate electrostatic field; and the field for each electron is obtained by adding the densities u_i^2 for all the other electrons, and finding by electrostatics the field of this charge and of the nuclei. Thus this field is self-consistent in the sense of Hartree; the result is a generalization of his method to more complicated problems than atomic ones.

For atoms, Hartree's procedure differs in the one detail that instead of taking the field so obtained (which would not be quite spherically symmetrical), he averages over all directions, to get a real central field for each electron to move in. This process also can be partly, although not entirely, justified by variation methods. If one demands that the functions u_i be solutions of a central field problem—that is, that they be products of spherical harmonics of the angles, by functions of r—and vary only the function of r, then one finds that the potential should be averaged over all orientations; but with a certain weighting function, not used by Hartree, depending on the spherical harmonic occurring in the wave function of the electron for which we are finding the potential. That is, Hartree's method could be slightly changed in this matter, with slight improvement of the results; but, except for this, it is definitely the best method, in the sense of variation principle, using central fields.

Closer examination shows that the potential we have found differs from Hartree's merely in being slightly dependent on the m, as well as the n and l, of the electron one considers. As a result, the energy levels of the different electrons of the same n and l, but different m, will differ slightly, an effect without physical meaning. In an earlier paper of the writer (Phys. Rev. **32,** 343, 1928), it is shown that essentially this same dependence on m results in only a small error, and further, that this effect has a very close connection with the resonance terms, and that by considering these also, the energy again becomes independent of m. It would therefore not be sensible to make this slight improvement in Hartree's method without at the same time making the more important one of considering resonance. If one wished to do this, one could again use variation methods, to derive a new method similar to self-consistent fields: one would demand that the wave function be written not as $u_1(x_1) \cdots u_n(x_n)$, but as a linear combination of such functions with permuted indices, so arranged as to have proper symmetry relations; and one would then vary the u_i's to make the energy a minimum. This would give a method similar to Hartree's, but really an improvement on it. Some preliminary calculations by Drs. Zener and Guillemin indicate that it may really be feasible to carry through this improvement. Their method differs from that sketched here only in that they represent the u_i's by simple analytic forms containing parameters, which they vary, instead of determining them by numerical solutions of a differential equation.

J. C. SLATER

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December 19, 1929.

An X-Ray Study of Molecular Orientation in the Kerr Effect

Perhaps the most successful theory of the Kerr effect for liquids is that which assumes a tendency toward definite orientation of the molecules under the influence of an electric field. Such a tendency towards uniform orientation should affect the x-ray diffraction pattern of the liquid by increasing the intensity of the x-rays observed at the peak of the diffraction curve. It is the purpose of this experiment to investigate the existence of such an effect.

Since, in observing the Kerr effect, the light beam is at right angles to the applied field it was thought best to arrange the path of the x-ray beam as nearly at right angles to the applied field as possible. In order to accomplish this the following method was devised. The liquids used were placed in a cylindrical glass cell one end of which was covered by a thin window of cellophane on whose inner side thin aluminum leaf was fastened. A beam of unfiltered x-rays from a molybdenum tube operated at 35 K.V. was reflected from this face, the cell replacing the crystal of an ordinary Bragg spectrometer. Measurements of the intensity of the reflected beam were made in the ordinary manner used in crystalline reflection, namely by turning the cell through

an angle θ, and the ionization chamber through 2θ, where θ is the grazing angle of incidence on the cell. The intensity of the reflected x-rays from an empty cell was less than 15 percent of the intensity observed at the same angle when the cell was filled. Soller slit sets were used to collimate both the incident and reflected beams. The reflection curves obtained for benzene and nitrobenzene were found to be practically the same as the corresponding liquid diffraction curves obtained by other methods.

The Kerr effect is most strongly shown by nitrobenzene when a rapid succession of practically instantaneous sparks are passed through it. Since full-wave rectification was used in obtaining the high potential for the x-ray tube it was thought desirable to synchronize the electric impulses across the cell with the peaks of the x-ray pulses. This was done by connecting a water rheostat in parallel with the tube, and connecting the aluminum leaf of the cell to this rheostat. In order to sharpen the electric impulse across the cell a spark gap was inserted between the rheostat and the cell, and a jet of air was blown between the balls of this gap. The other end of this cell was covered with a grounded brass plate.

All observations of the effect of the electric field were made with the cell at the grazing angle corresponding to maximum reflected intensity. Readings were taken alternately with and without a field of 13 K.V. per cm across the cell. Four groups of readings of 25 pairs each were obtained for nitrobenzene, the increases in intensity being 1.8, 2.5, 2.1, and 2.9 percent respectively for each of the four groups. The average increase with the field was thus found to be 2.3 percent, with a probable error of 0.5 percent. The effect thus observed is between four and five times the probable error.

With a field applied to the cell in the manner described above benzene shows little or no Kerr effect. Hence, if the Kerr effect is due to partial molecular alignment, benzene —under the field applied to nitrobenzene— would not be expected to show a change in intensity of the peak maximum. Four groups of readings of 25 pairs each, taken alternately with and without the field in precisely the same manner as nitrobenzene, showed for benzene changes in intensity of -0.4, $+0.3$, -0.3, and -0.6 percent. The negative sign is used to indicate the variations in the opposite direction to that of nitrobenzene. The average change in intensity for all readings is -0.3 percent which is well within the probable error. This lack of any definite shift in intensity with the field rules out the possibility that the effect observed for nitrobenzene might be due to a slight bending of the cellophane window as a result of electrostatic forces of attraction.

The results here given show for nitrobenzene an increase in intensity of the peak maximum of an amount that is approximately five times the probable error, while for benzene any change observed lies not only well within the probable error but also is, for the most part, in a direction opposite to that of nitrobenzene. It would thus seem that for nitrobenzene there occurs, when the proper type of electric field is present, a small but detectable tendency of the molecules to align themselves in a common direction.

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December 21, 1929.

A Comparison of the Reflection Spectra of $SmCl_3 \cdot 6H_2O$ at Room Temperature and at that of Liquid Air with its Absorption Spectra at Low Temperatures

In a communication to Nature[1] we discussed a change which we observed in the absorption spectrum of a single crystal of $SmCl_3 \cdot 6H_2O$ as we lowered the temperature to that of liquid hydrogen. Many lines or bands which were prominent in the spectrum at room temperature practically disappeared at the temperature of liquid hydrogen and others which were extremely faint increased in intensity as the temperature was lowered. We ascribed this change in relative intensity to the presence of different electronic configurations of Sm^{+++} in the solid state in thermal equilibrium. (This interpretation is in accord with the magnetic behavior of Sm^{+++}.)

At present we wish to report the most general features of the reflection spectra

[1] Freed and Spedding, Nature, April 6 1929).

obtained by reflecting a continuous spectrum from the surfaces of many small crystals of the same salt. The reflected spectrum has the characteristics of an absorption spectrum. The lines which we attribute to the electronic modification stable at the low temperature, that is those which are prominent only at the *low* temperatures in absorption are found relatively much more intense at *room temperature* in reflection. In addition, the lines in the reflection spectra are accompanied by satellites about 160 cm^{-1} toward the red. The reflection spectrum at room temperature also contains narrow diffuse bands which were not observed in absorption.

At the temperature of liquid air, these bands sharpen and become resolved into multiplets consisting of very narrow lines. At this temperature, many new lines make their appearance and they tend to cluster on both sides of the lines which are found in the absorption spectrum. Satellites accompany the prominent lines at intervals of about 160 cm^{-1} at the temperature of liquid air also.

Our method of photographing the reflection spectra does not exclude the simultaneous appearance of the absorption spectrum. (We intend to eliminate this spectrum in our future work.) However, the astonishing intensification of the "low temperature" lines in the reflection spectrum at room temperature cannot be ascribed to any spurious experimental influence because we are considering relative intensities only.

A fluorescence or an unusual reflecting power appears to take place on the violet side of a number of the lines in the reflection spectrum at the temperature of liquid air which do not occur in absorption.

The force fields in the surface are definitely different from those within the crystal. It is conceivable that in the surface there is a higher concentration of the "low temperature modification" than corresponds to an equilibrium distribution within the crystal. It is also possible that the absorption coefficient of this particular modification may be greater under these conditions.

The large number of entirely new lines which occur in the reflection spectrum may possibly be due to the fact that the electrostatic fields to which the Sm^{+++} ions within the crystal are exposed are no longer regular in direction and in magnitude in the surface so that any "forbidden" electronic jumps within the crystal are no longer "forbidden" in the surface. In other words, the probability of transition between certain states has been increased. We are investigating this phenomenon further.

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December 19, 1929.

An Observed Periodicity in the Packing Fraction

It is found that a single oscillatory curve can be fitted to the packing fraction data taken by Aston, eliminating the necessity of the two branches at the small mass number end (Proc. Roy. Soc. **A115,** 487 (1927)). Points of maxima are located at mass numbers 6, 10, 13, 17, 21, 25, $\cdots$, and minima are found for the elements whose mass number is an integral multiple of four.

The mass number of the atom was assumed to be given by the expression $4n+x$, where $n=0, 1, 2, 3, \cdots$ and $x=1, 2, 3$ or 4. Since the packing fraction represents an average mass defect per proton it is evident that in the $4n+1$ type of atom, the one proton is loosely connected to the core of the nucleus probably existing as a satellite in the form of a neutron. In the $4n+2$ type the two protons are a little more tightly bound to the core. Similarly for the $4n+3$ atom. And finally for the $4n+4$ type of atom we find maximum packing, the four protons probably forming an alpha-particle which goes into the center of the nucleus. These conclusions were arrived at after a calculation of the change in packing fraction per proton produced by the "x" portion of the atom had been made wherever possible. Curves were plotted showing the effect of the value of "x" on this change in the packing fraction, these being used to determine the points of maxima and minima.

The fact that the packing becomes greater for the $4n+4$ atoms with an increase in mass number indicates that the alpha-particle actually goes into the center of the nucleus each time "x" becomes eqnal to four. This

was suggested by Aston. This continues up to about mass number eighty. A definite oscillation for the kryptons is observed. For the heavier elements the data are not accurate enough to show any oscillation if it is present. Aston has attributed the general rise in the curve beyond mass number eighty to the increasing complexity of the nuclear structure. If this oscillation continues for the heavier elements, we might still have the alpha-particle forming in the nucleus as before but instead of going into the center they begin to form satellites around the now "filled up" center of the nucleus. For the heaviest elements these satellites may be far enough from the core to render them unstable and thus produce atomic disintegration with the ejection of alpha-particles and electrons. More accurate packing fraction data are needed to determine definitely whether this periodicity exists for the heavy elements.

HOWARD OLSON

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January 13, 1930.

The Unified Field Equations and Schwarzschild's Solution. II.

All of the implications of Eq. (1) of the previous note[1] have since been worked out. Another consequence of the case $\alpha=\beta$ ($\alpha, \beta=1, 2, 3$) is

$$\frac{W''}{UW}+\frac{W'}{Wr}\left(\frac{2}{U}+\frac{1}{U^2}-\frac{U'r}{U^2}-1\right)-\frac{U'}{U^2r}+\frac{1-U}{U^2r^2}=0. \quad (1)$$

The only other non-trivial case so far not considered is $\alpha\neq\beta$ ($\alpha, \beta=1, 2, 3$); this yields

$$\frac{W''}{UW}+\frac{W'}{Wr}\left(\frac{2}{U}-\frac{2}{U^2}-\frac{U'r}{U^2}-1\right)-\frac{U'}{U^2r}-\frac{2(1-U)}{U^2r^2}=0. \quad (2)$$

If for U is substituted the solution obtained in the previous note

$$U=1/(1-m/r),$$

both (1) and (2) are seen to have as a particular solution

$$W=C\left(1-\frac{m}{r}\right), \quad (3)$$

where C is a constant. On subtracting (2) from (1) and reducing, we get

$$W'r=W(U-1)=\frac{mW}{r-m} \quad (4)$$

which was found in the previous note as a consequence of the case $\alpha=\beta$ ($\alpha, \beta\neq4$). The general solution of (4) is (3); and if the reasonable boundary condition

$$\lim_{r\to\infty} W=1$$

is applied—the corresponding condition is already satisfied by U—, the constant C becomes unity, and we find, unambiguously,

$$W=1-\frac{m}{r}.$$

MEYER SALKOVER

University of Cincinnati,
January 11, 1930.

[1] See page 209, this issue.

On the Vibration Frequencies of HCl and HBr in the Liquid State

Modified scattering of the mercury 4047 line by HCl in the liquid has already been reported (Science, March 29, 1929). We have repeated our measurements with greater accuracy and have also measured a modified line from liquid HBr, at −75°C. Calling ν_1 the observed modified line, ν_0 the molecular frequency and λ_0 the corresponding wavelength, the results are (reduced to vacuum):—

Liquid	ν_1	ν_0	λ_0
HCl	21924	2781	3.595μ
HBr	22226	2479	4.033μ

The value of ν_0 for gaseous HCl is 2886 (Wood, Phil. Mag. **7,** 744 (1929); Colby, Phys. Rev. **24** (1), 53 (1929)), and for gaseous HBr is 2559 (Imes, Astrophys. J. **50,** 251 (1919)). Comparing these with the above values, we see that ν_0 is shifted to the smaller frequencies in the liquid, 105 wave-numbers in the case of HCl and 80 in the case of HBr.

The Lorentz-Lorenz theory affords an explanation of frequency differences of a molecule in different physical states (see e.g. Wolf and Herzfeld, Handbuch der Physik).

Thus, letting ν_0' refer to the liquid, there is the relation

$$\nu_0' = \left(\nu_0^2 - \alpha \frac{Ne^2 p}{m}\right)^{1/2}$$

where N is the number of molecules per unit volume in the liquid, p the number of resonating particles of charge e and mass m in a molecule, and α times the polarization per unit volume is the Lorentz force, α being $4\pi/3$ for a spherical cavity. But α when calculated from the above observed frequencies in the gas and in the liquid comes out not around $4\pi/3$ but 0.20 for HCl and 0.16 for HBr. In fact, using $4\pi/3$ for α makes the last term larger than ν_0^2 for these molecules.

However, this calculation is made with 4.77×10^{-10} e.s.u. for e, that is, it assumes that the vibrating atom is H^+. But we know that HCl and HBr do not have this structure. Dennison has, indeed, introduced into band spectrum theory the "effective charge," which he finds for HCl to be $0.199\times4.77\times10^{-10}$ e.s.u (Phys. Rev. **31,** 503 (1928)). Using this value for e, and retaining $\alpha=4\pi/3$, we now calculate $\lambda_0'=3.578\mu$, in quite good agreement with our measured 3.595μ.

These results and others will be presented at greater length later.

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A. SANDOW

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January 13, 1930.

The Reflecting Powers of Atoms for X-rays of Different Wave-lengths

In the course of measurements of atomic F-curves[1] experiments have been made to find out whether the scattering power of an atom changes with the wave-length of the x-rays used. It might be expected that such a wave-length effect, if it exists, would be most conspicuous in the neighborhood of characteristic frequencies of the diffracting atom. With this in mind, the F-curves of NiO have been mapped for molybdenum, copper and nickel radiation and points have been determined upon the curves of the metals iron, copper and nickel for molybdenum, copper, nickel and iron rays. This has been done by comparing the relative intensities of powder lines from these substances with the intensity of a standard NaCl reflection. Though the scattering powers thus obtained are not necessarily correct in absolute value, nevertheless as long as the F of the standard NaCl reflection is either constant or changes in a regular fashion with increasing wave-length, the relationships they show amongst themselves will be significant.

Earlier measurements from this laboratory[2] have shown that the scatterings of metallic iron and copper for copper K-radiation are less than for the $K\alpha$ line of molybdenum. Additional observations have shown (1) that the scattering power of a particular atom decreases with increasing wave-length as this wave-length approaches a critical excitation value for the scatterer; (2) that F is a minimum for this longest exciting radiation; (3) that this number then rises to a maximum for a wave-length equal to that characteristic of the scatterer; and (4) that thereafter it appears to fall slowly with further increase in wave-length. Thus, for example, the approximate values of Table I are obtained assuming $F(220, \text{NaCl})=15.62$.

TABLE I.

Wave-length	Fe $F(110)$	Ni $F(200)$	NiO $F(220)$	Cu) $F(220$
Mo $K\alpha$	15.87*	—	18.28	14.28*
Cu $K\alpha$	11.48	13.70	15.83	11.53
Ni $K\alpha$	9.77	14.48	16.88	11.18
Fe $K\alpha$	13.45	—	—	—

* See footnote 2.

The absorption coefficients of the diffracting powders enter into these determinations. The sequence of Table I is obtained, however, whether either experimental coefficients are used or those calculated by the general formula of Jönsson.[3]

The usual theory of the intensity of reflection from ideally imperfect crystals, to

[1] C. G. Darwin, Phil. Mag. **43,** 800 (1922); etc.; A. H. Compton, X-rays and Electrons (New York, 1926) Chap. V.

[2] A. H. Armstrong, Phys. Rev. **34,** 931 (1929).

[3] E. Jönsson, Uppsala Univers. Årsskrift, 1928.

which these data are legitimately referable indicates that F, the ratio of the scattering of an atom to that of a single electron, may be expected to be constant for constant values of $\sin\theta/\lambda$. In other words, it will be the same for a particular reflection no matter what wave-length is employed.

The observed departures from this constancy probably have more than one cause. Thus the minimum in F which occurs at the critical absorption wave-length of the scattering atom is most naturally accounted for if energy which otherwise would be coherently scattered is utilized in the production of the secondary radiation. At the same time, the fact that maxima in F are always obtained at characteristic wave-lengths of the scatterer suggests some sort of resonance. Such resonance, if it exists, cannot be sharp, however, for F falls away only slowly with longer wave-lengths.

It is apparent that photographs of RbBr made by Mark and Szilard[4] with strontium and bromine radiations are expressions of variations in F of the same nature as those just described.

Detailed results of these experiments will be published soon.

RALPH W. G. WYCKOFF

Rockefeller Institute for Medical Research,
New York City,
January 7, 1930.

[4] H. Mark and L. Szilard, Zeits. f. Physik. **33,** 688 (1925).